



A critical review on latest innovations and future challenges of electrochemical technology for the abatement of organics in water

Carlos A. Martínez-Huitle^a, Manuel A. Rodrigo^b, Ignasi Sirés^{c,*}, Onofrio Scialdone^d

^a Instituto de Química, Universidade Federal do Rio Grande do Norte, Campus Universitário, Av. Salgado Filho 3000 Lagoa-Nova, CEP59078-970 Natal, RN, Brazil

^b Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies, Ciudad Real, Universidad de Castilla-La Mancha, Ciudad Real 13071, Spain

^c Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Ciència de Materials i Química Física, Secció de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

^d Dipartimento di Ingegneria, Università degli Studi di Palermo, Palermo 90128, Italy

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ABSTRACT

Updated water directives and ambitious targets like the United Nations' Sustainable Development Goals (SDGs) have emerged in the last decade to tackle water scarcity and contamination. Although numerous strategies have been developed to remove water pollutants, it is still necessary to enhance their effectiveness against toxic and biorefractory organic molecules. Comprehensive reviews have highlighted the appealing features of the electrochemical technologies, but much progress has been made in recent years. In this timely review, a critical discussion on latest innovations and perspectives of the most promising electrochemical tools for wastewater treatment is presented. The work describes the performance of electrocatalytic anodes for direct electrochemical oxidation, the oxidation mediated by electrogenerated active chlorine, the electrocatalytic reduction as well as coupled approaches for synchronous anodic and cathodic processes combined with homogeneous and heterogeneous catalysis. The last section is devoted to the assessment of scale-up issues and the increase in the technology readiness level.

1. Introduction

In recent years, process intensification has boosted many large-scale human activities, from the primary sector to industrial manufacturing, giving momentum to the global economy. Such expansion has revealed its darkest side, evidenced by a non-environmentally friendly development as is well exemplified by the many freshwater resources put at risk. A key factor to explain this imbalance between economic growth and environmental preservation is the inefficacy of the existing water treatment technologies to remediate the pollution of aqueous effluents contaminated by toxic and refractory organic contaminants. Within this framework, environmental electrochemical technology has shown great potential to ensure their fast and complete degradation, thanks to electrocatalysis and homogeneous and heterogeneous catalysis phenomena, and to effectively contribute to the sustainable development of modern societies. Indeed, the Sustainable Development Goals (SDGs), listed in the United Nations 2030 Agenda, encourage a more respectful and inclusive world transformation and water constitutes the core of some of the SDGs because, owing to its scarcity, new policies on its reuse

are required worldwide. In this sense, the development of technologies and smart water solutions will play a key role in achieving the SDG 6 dedicated to clean water and sanitation, since these represent a substantial opportunity if their implementation is carried out to guarantee sustainability and increase competence in all water sectors, offering a coherent vision for the future.

Research on new materials and reactors has enhanced the effectiveness and efficiency of electrochemical water treatment technologies. These are finding their niche as reliable alternatives to more conventional biological and physicochemical methods, as well as to classical advanced oxidation processes (AOPs) like ozonation, heterogeneous photocatalysis, Fenton process or wet oxidation. In particular, several flexible, modular, nearly autonomous electrochemical systems, which in addition can be combined with renewable energy, have been developed.

In the last six years, several authors have addressed different critical issues of electrochemical water treatment technologies such as the energy consumption, which had historically hindered the progress in the environmental electrochemistry field. As a result, processes like direct electrochemical oxidation (EO), indirect electro-oxidation (IEO),

* Corresponding author.

E-mail address: i.sires@ub.edu (I. Sirés).

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electroreduction (ER), and electro-Fenton (EF), among others, are nowadays very appealing for the treatment of wastewater. Worth mentioning, the effectiveness of these processes is primarily linked to the electrocatalytic reactions occurring either at the anode (e.g., EO, IEO) or the cathode (e.g., ER) surface. Additionally, some authors have also developed various coupled processes that benefit from the utilization of both types of reactions (e.g., EF).

In 2015, the authors published a critical review on the most promising electrochemical tools for the treatment of wastewater contaminated by organic pollutants [1]. The fundamental aspects of selected processes were discussed in detail, with the main aim to evaluate the prospects for a wider distribution and penetration in the market. Although key advantages of these technologies were highlighted and supported with a large set of studies, relevant shortcomings that had impeded a more global full-scale implementation were identified. Since 2015, many relevant innovations have been developed and described in the literature, significantly strengthening these technologies, which has made them mature enough for long-term application to actual water treatment. The growing interest is evidenced by a search in Scopus database using “electrochemistry and wastewater” as keywords, which yielded 4252 documents until 2015, and 6729 from 2016. As a more specific example, the research carried out using “electro-Fenton” as keyword yielded 727 and 1689 results before and after 2016, respectively. Readers interested in a deeper analysis of bibliometric data can check recently published works, dedicated either to electrochemical degradation of organic pollutants [2] or focused on a specific process like EF [3].

In this work, an update of our previous review is presented, offering a critical discussion on the advantages and disadvantages of latest innovations and, more in general, on the current perspectives of the most promising electrochemical tools for wastewater treatment. This is not a mere summary of published results; beyond that, weaknesses and strengths of the reviewed processes are highlighted. Focus is put on purely anodic, purely cathodic and coupled anodic-cathodic processes. Furthermore, the innovations on materials and reactors and the particularities arising from upscaling have been discussed in detail, including the powering of these electrochemical technologies using green sources and the key economic aspects. In conclusion, the review provides an updated, concise, and critical evaluation of such processes and setups, as well as the main innovations, also paying attention to the future work required for reaching the implementation at industrial scale or the commercialization of specific electrochemical devices. In particular, Section 2 is focused on direct EO, Section 3 discusses the IEO mediated by electrogenerated active chlorine, Section 4 describes the use of cathodic processes and their promising coupling with anodic processes, whereas Section 5 is devoted to the scale-up and increase in the technology readiness level of electrochemical processes for the treatment of wastewater. Finally, a brief commentary on how the Nexus sectors can be benefited by achieving SDGs with electrochemical-based solutions, is given.

2. Anodic oxidation of organic pollutants

Anodic oxidation (AO), electrooxidation or electrochemical oxidation (EO), as is commonly named the most popular and simple electrochemical technology for the degradation of organic pollutants contained in water, is the favorite approach among the electrochemical advanced oxidation processes (EAOPs) [1]. In fact, this electrolytic technology has proved its effectiveness to mineralize a large number of organic compounds in different water matrices, either synthetic or made with actual wastewater. However, the EO efficacy, in terms of water disinfection/decontamination, depends on the chemical and physical features of the electrocatalytic material (i.e., the anode) as well as on various operative conditions. This has determined and limited its full implementation as a method at industrial scale, but, at the same time, these disadvantages have led to new challenges and opportunities in the

last decade (see Fig. 1). The anode material determines the amount, the nature and the oxidation power of the electrogenerated oxidants. Meanwhile, the operation conditions can have influence on the most important advantages of the EO approach, such as versatility, amenability to automation, viability under mild conditions, moderate energy consumption and minimized cost. Generally speaking, poor or incomplete knowledge on electrocatalysis fundamentals and technological concepts has created significant and numerous myths, controversies and misunderstandings regarding the EO technology, which has repeatedly caused mistakes while planning investigations or during the scientific interpretation of the experimental behaviors observed. Several of these controversies and misunderstandings are detected during the peer-review process of countless manuscripts, being possible to amend them before their publication. Also, incorrect concepts and myths are found in oral and poster communications during electrochemical and engineering meetings. The controversies are related, for example, to the type of the oxidants formed (radical and nonradical) and the mechanism followed for their production, as well as the nature of the electrocatalytic materials that may favor the direct electrogeneration of specific oxidants or their formation via the participation of hydroxyl radicals or other activation approaches. On the other hand, the form in which the catalytic reactions proceed, either as surface-layer or as volume-chemical reactions, has caused fundamental misunderstandings because not all the oxidizing species participate equally in the degradation of organics. This, despite being apparently obvious, depends on the nature of the anode and the electrochemically produced oxidants, as well on their properties. It is essential to take into consideration that, when different oxidants are produced (i.e., radical vs. nonradical), key parameters need to be evaluated: extinction time, reactivity, chemical structure, parallel reactions (scavengers and self-decomposition reactions). In turn, this has created myths, as for example the univocal anodic electroactivity towards the organics or oxidants. Nonetheless, it has been confirmed that there are electrodes with hybrid behaviors, even in cases when these are made of the same material. Other important aspects include: the distinction between the developed mechanisms, the identification of oxidants and their oxidative action, which can take place close to the anode surface or in the bulk, depending on their extinction time. For this reason, the description and discussion of the models that illustrate the EO technology should be reconsidered. This section is focused on recent advances achieved since 2015, considering the fundamentals of the EO treatment of organic pollutants in water.

First, attention is paid to a short description of the most accepted “model” and accurate electrode/solution interface representations, being immediately followed by the insights and novelties currently reported in the literature as well as on the advances in the mechanisms. Thereafter, the use of different anodic materials is critically discussed and then, focus is put on the electrochemical systems employed in EO and the problems to be overcome for reaching a full-scale implementation. Complementary discussions on the content addressed in this section can be found in the related section of our previous review [1], although now more details are given on the basis of the most novel scientific achievements and developments.

2.1. Fundamentals and advances in understanding the electrocatalytic mechanisms, production of reactive oxidizing species and next challenges

Pioneering studies on the EO process, as an emerging alternative for wastewater treatment, started in the 70 s (Fig. 1). All researchers dedicated relevant efforts to study the behavior of different anodic materials (focusing on their electrocatalytic activity and electrochemical stability) by oxidizing different organic pollutants, predominantly phenolic compounds and aliphatic acids. In contrast, the course (or mechanisms) of the EO, in which the organic pollutants are completely degraded or selectively converted to other molecules, was a key task in the 90 s (Fig. 1). In fact, the importance of anodic discharge of H₂O in anodic oxygen-transfer reactions and its electrocatalysis (water discharge as a

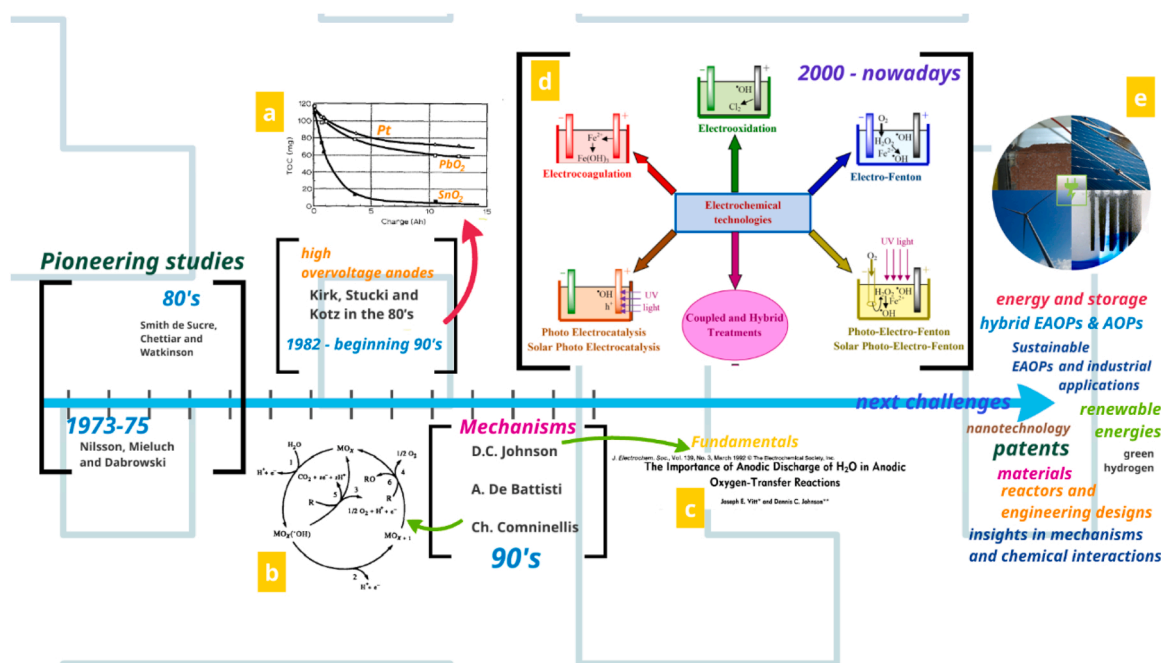


Fig. 1. Advances on the EO technology: pioneering studies, investigation on anodes, fundamentals and initial mechanistic contributions, advances on electrochemical technologies and next challenges and opportunities of EO (some of them are also valid for other electrolytic treatments reviewed in next sections).

(a) Adapted with permission from [4]. Copyright 1991 Elsevier B.V. (b) Adapted with permission from [5]. Copyright 1994 Elsevier B.V. (c) Adapted with permission from [6]. Copyright 1992 Elsevier B.V. (d) Adapted with permission from [7]. Copyright 2015 Elsevier B.V. (e) Adapted with permission from [8]. Copyright 2018 Elsevier B.V.

prerequisite of anodic O-transfer mechanisms from hydroxyl radicals concurrently with O_2 evolution) was initially described in the beginning of the 90 s by Johnson's group [6,9–12]. After that, Comninellis [5] completed the studies of water discharge, as well as the electro-generation of hydroxyl radicals at different electrodes. He presented a simplified mechanism for the EO or electrochemical combustion of organics, according to which selective oxidation is feasible with oxide anodes and combustion occurs at electrodes that favor the accumulation of hydroxyl radicals at their surface (Fig. S1 in Supplementary Material). This model has been constantly and repeatedly used in several reviews and books [1,13–27], generating positive and negative point of views as well as representations or adaptations that have created myths and misunderstandings. For example, on the one hand, the wrong model representation to illustrate the production of hydroxyl radicals and/or other oxidants at the anodic surface, omitting the Nernst layer dimensions. As a result, this causes misconceptions related to the oxidants, such as the incorrect understanding of the region in which each of them acts, the non-consideration of the extinction time, as well as the local pH conditions at the electrode vicinity and their effects on the nature of the oxidants in solution (e.g., active chlorine speciation). On the other hand, the possible co-existence of direct and indirect oxidation mechanisms at the same electrocatalytic surface, as well as the competition between the oxidizing species production and the additional activation reactions. At this point, it is worth highlighting that the initial models for EO were proposed under acidic conditions, which can cause controversies when specific oxidants are formed. Therefore, the importance of the advances related to the electrode material regarding the formation and reactivity of hydroxyl radicals and their models is described below.

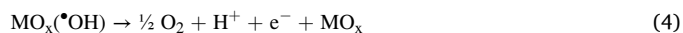
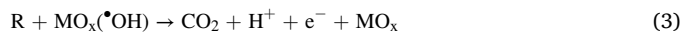
Based on the early Comninellis' model [5] (Fig. S1), which was reported in 1994 for selected oxide anodes (MO_x , including Pt, which under O_2 evolution is presented as PtO_x , Ti/IrO_2 , Ti/SnO_2), the electrochemical conversion or combustion of organic compounds occurs upon water discharge as first step producing adsorbed hydroxyl radicals (reaction (1)):



As a second step, an interaction between the adsorbed hydroxyl radicals and the oxygen already present in the oxide anode, may be achieved, forming the so-called higher oxide MO_{x+1} due to a possible transition of oxygen from the radical to the oxide lattice (reaction (2)).



Two states of "active oxygen" can be considered, corresponding to (i) physisorbed "active oxygen" (adsorbed $(\bullet OH)$) and (ii) chemisorbed "active oxygen" (oxygen in the oxide lattice). The physically and chemically adsorbed "active oxygen" should favor different routes in the presence of oxidizable organic compounds [5]. The former predominantly promotes the complete combustion of organics (reaction (3)) in concomitance with O_2 evolution (reaction (4)). Meanwhile, the conversion of organics should be selectively caused in the latter (reaction (5)), with simultaneous formation of O_2 (reaction (6)).



These route-reactions were summarized in a general scheme (Fig. S1). Nevertheless, it was only after the investigations with other electrocatalytic materials ($Ti/SnO_2-Sb_2O_5$, PbO_2 and boron-doped diamond (BDD), at the end of the 90 s), that it was possible to use the model to distinguish two limiting cases, active and non-active anodes [17,18]. This classification was dependent on the kind of interaction between the anode surface and the hydroxyl radicals electrochemically generated via water discharge, as well as on the potential for oxygen evolution presented by each electrode. Thus, it was demonstrated that the nature of the electrode material influences strongly both, the selectivity and the efficiency of the process [1,5,16,17,22].

These observations were useful to improve the comprehensive model in the year 2003 by Comninellis [18] (Fig. S2) including not only oxides

anodes. Moreover, direct oxidation by a direct electron transfer to the anode, ending in a poor wastewater depollution, was also considered. Mediated oxidation by the electrogeneration of oxidizing species (which are constantly generated) from water discharge or supporting electrolyte oxidation at high applied current (I_{appl}) can be observed as well, reaching a partial or total decontamination.

It is assumed that the heterogeneous formation of physisorbed hydroxyl radicals ($M(\bullet\text{OH})$) is attained at the surface of active and non-active anodes (which are denoted as M) by the oxidation of water from reaction (7). Subsequently, the heterogeneous $M(\bullet\text{OH})$ interact strongly or weakly with the anode surface, respectively [18].



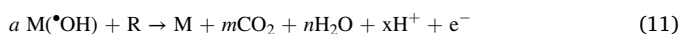
For active anodes, a strong interaction of the hydroxyl radicals with the electrode surface is attained, forming the higher oxides or superoxides from reaction (8), which are denoted as MO in this model, while only $M(\bullet\text{OH})$ is produced from reaction (1) at non-active anodes because a weak interaction between the hydroxyl radicals and the electrode surface is accomplished.



It is important to point out that MO is formed as chemisorbed “active oxygen” when higher oxidation states are available at the M surface, above the standard potential for oxygen evolution ($E^\circ = 1.23$ V vs. SHE) [17–19]. After that, it participates as mediator via reaction (9) in the selective oxidation of organics (so-called electrochemical conversion), which occurs in concomitance with oxygen evolution (reaction (10)), as side reaction, affecting the efficiency of the EO process.



Meanwhile, the direct reaction of physisorbed $M(\bullet\text{OH})$ or free $M(\bullet\text{OH})$ with organic molecules leads to their electrochemical incineration (CO_2 and water) by reaction (11):



where R is an organic compound with m carbon atoms and without any heteroatom, which needs $a = (2m + n)$ oxygen atoms to be totally mineralized to CO_2 . This reaction competes with the side reaction of O_2 evolution given by reaction (12), which can significantly affect the efficiency of the electrolytic treatment [18,19].



Fig. S2 exemplifies the reaction scheme of the proposed model in acidic medium, where M designates an active site at the anode surface [18]. According to the model, it was in theory defined that, in the reaction cage [28] or close to the Nernst layer:

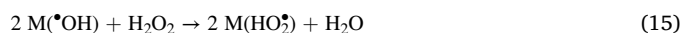
- (i) no direct participation of the non-active anodes is expected in the anodic reaction with organic molecules because these do not provide any catalytically active site for adsorption of reactants and/or products in aqueous medium. In other words, the only possible anodic reactions are, in principle, the outer sphere reactions and water discharge. In the former, no strong interactions from the reactants and products with the electrode surface are accomplished, whereas the H_2O molecules cover the electrode surface, with at least one adsorbed layer, in the latter, being electrolyzed. In the meantime, the heterogeneous hydroxyl radicals produced from water discharge, which are involved in the oxidation of organic pollutants, promote the electrochemical incineration or combustion [5,18];
- (ii) direct interaction between organic molecules (reactants or products) and the anode surface is reached at active anodes. Hence, there is chemisorption of the organic molecules; higher

oxidation states are available, above the thermodynamic potential for oxygen evolution, at the anode surface. This is due to the electrocatalytically active sites that are provided by active anodes. In this context, the surface redox couple MO/M can act as a mediator in the oxidation of organic molecules at the anode surface, favoring a selective oxidation or electrochemical conversion [5,18,19].

Therefore, generally speaking, the bond strength between the anode (M) and $\bullet\text{OH}$ is directly associated to the chemical reactivity (i.e., rate of oxidation of the organic compounds with electrogenerated hydroxyl radicals) and the electrochemical activity (i.e., overpotential for oxygen evolution), which allows establishing a general rule: “Weak $M(\bullet\text{OH})$ interactions lead to low anode electroactivity (i.e., high O_2 -overvoltage anodes) and high anode reactivity (fast chemical oxidation of the organic molecules)” [18]. However, this is not completely true for all the electrocatalytic materials because some novel anodes developed have shown the co-existence of both direct and indirect oxidation approaches, as detailed in the Section 2.2.2.

Over time, it was also found that a great variety of heterogeneous oxidizing species can be formed from water discharge and other oxidant precursors [8,22,29–34], such as reactive oxygen species (ROS) (e.g., H_2O_2 , O_3), peroxocompounds (peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$), peroxodicarbonate ($\text{C}_2\text{O}_6^{2-}$) and peroxodiphosphate ($\text{P}_2\text{O}_8^{4-}$) and active chlorine, among others. This favors a selective (electrochemical conversion) or complete (electrochemical combustion or electrochemical incineration) oxidation of the organic pollutants in wastewater. Several advances on strategies to identify the oxidizing species have been reported in the last years [30,35], which facilitates the understanding of the influence of experimental factors on their production, as explained below.

Note that H_2O_2 is formed by dimerization of $M(\bullet\text{OH})$, either close to the anode surface via reaction (13) or in the reaction cage via reaction (14); alternatively, this oxidant can be formed via cathodic reactions (Section 4). The reaction of H_2O_2 with free heterogeneous $\bullet\text{OH}$ yields the weaker oxidant hydroperoxyl radical ($M(\text{HO}_2^\bullet)$) via reaction (15) [1,22,36–39].



From anodic water discharge, another weaker oxidant like O_3 ($E^\circ = 1.51$ V vs. SHE) can also be generated via reaction (16) [40].



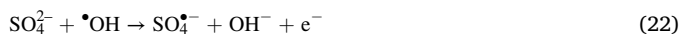
However, the main ROS that participates in the degradation of organic molecules is the free heterogeneous $\bullet\text{OH}$, much stronger than H_2O_2 , $M(\text{HO}_2^\bullet)$ and O_3 , although these oxidants also become relevant in the EO technology in the absence of chloride or when low concentrations of sulfates, phosphates and carbonates are present in the water matrices.

Concerning the peroxocompounds ($\text{S}_2\text{O}_8^{2-}$, $\text{C}_2\text{O}_6^{2-}$ and $\text{P}_2\text{O}_8^{4-}$) [31], which are weaker oxidizing species, these can be also formed, in parallel, with ROS from the corresponding anodic oxidation of SO_4^{2-} or bisulfate by reaction (17), HCO_3^- by reaction (18) and PO_4^{3-} by reaction (19).



$\text{S}_2\text{O}_8^{2-}$ is also synthesized by dimerization of the sulfate radical anion ($\text{SO}_4^{\bullet-}$), which is a strong oxidant [41,42]. The generation and concentration of $\text{SO}_4^{\bullet-}$ are determined by the pH conditions and the anodic

surface (the formation of $\text{S}_2\text{O}_8^{2-}$ and $\text{SO}_4^{\bullet-}$ has only been confirmed at few electrodes, such as doped and suboxides of Ti, Pb-based oxides as well as BDD) [27,31,43], which favor the participation of free heterogeneous $\bullet\text{OH}$, as follows:



When the water matrices or solutions contain chloride, a different type and number of oxidizing species are produced [7,25,29,33,44]. This EO approach is commonly named electrochemical Cl-mediated oxidation, oxidation with active chlorine or indirect EO by chloride oxidation, which is considered a volume-based chemical oxidation approach and turns out to be more significant than mediated oxidation by free heterogeneous $\bullet\text{OH}$ (see Section 3). Actually, it is due to the extinction time of active chlorine species, which allows extending the action region of these oxidants out of the Nernst layer, in contrast to the adsorbed hydroxyl radicals. For that, their identification and quantification as well as their role should be investigated, mainly because the electrogenerated active chlorine species are formed from Cl^- oxidation at the anode as well as from chemical equilibria that depend on the pH conditions. This route will be described in detail in Section 3.

Afterwards, the examination of oxidants formation, the key role of oxidants mechanisms, their dependence on the anodic material used and the investigation of the parameters that have influence on the EO performance, as well as the pollutant degradation pathways and kinetics, have been extensively investigated and widely reported in the last years [1]. From these studies, significant advances have been accomplished, such as:

- i) understanding of the type, nature, quantity and mechanisms of production of reactive oxidizing species in EAOPs;
- ii) determination of the oxidant reactivity and elucidation of the intermediates generated during their oxidation, as well as the degradation pathways;
- iii) improvements on the formation of reactive species by controlling various factors (the type of the treatment technique, electrode/electrocatalyst materials, water/wastewater composition, pH conditions and operation parameters);
- iv) development of the techniques and operation parameters to produce single or multiple oxidants by using single or combined electrochemical processes;
- v) understanding of the power and reactivity of each oxidant, arising from their formation or reaction mechanisms (heterogeneous and homogeneous);
- vi) acquisition of knowledge about the activation of the electrogenerated oxidants;
- vii) prevention of the toxic species or substances;
- viii) advances on the techniques for detection of oxidizing reactive species;
- ix) use of oxidant solutions as ex situ treatments, commonly called off-grid technologies;
- x) development of green oxidants electrosynthesis powered by renewable energies.

However, the following important drawbacks can be also emphasized:

- i) limitations related to the lack of understanding about the fraction of direct and/or indirect oxidations;
- ii) restrictions about the use of the electrogenerated oxidants as in situ or ex situ oxidation approaches;
- iii) lower current efficiencies during the electrosynthesis of oxidants;

- iv) lack of information about the stability (half-life) of the reactive species;
- v) disparities in the effects of parameters when comparing the treatment of synthetic and actual water matrices, owing to the role of the matrix components and the presence of oxidant scavengers;
- vi) generation of recalcitrant organic byproducts;
- vii) oxidative restrictions due to the different anodic surface-layer-based or volume-based character of the reactive species.

As already stated above, several oxidant species (radical and non-radical) [29,30,35] can be produced by heterogeneous and homogenous catalytic approaches. In order to obtain a deeper electrochemical/chemical insight in this regard, it is imperative to address their identification and quantification (Fig. 2). This would allow the proposal of reaction pathways that demonstrate the participation of specific oxidants during the treatment of organic pollutants and/or waterborne agents as well as the design, development (translating from lab to prototype or pilot scales) and commercialization of specific electrochemical devices for decontamination or for production of oxidants to be used in ex situ applications.

The identification and quantification of nonradical and radical oxidizing species is achieved by direct or indirect instrumental analysis, coupled or not to chemical reactions (e.g., scavenging techniques) [30]. In the former case, nonradical reactive species such as Cl_2 , HOCl , ClO^\bullet , ClO_2 , $\text{S}_2\text{O}_8^{2-}$, $\text{C}_2\text{O}_6^{2-}$ and H_2O_2 formed by EO are preferentially monitored using chromatographic, colorimetric and titrimetric methods [29,36,45–47]. For a general screening of the type and concentration of the oxidants homogeneously or heterogeneously generated by EO technology, the colorimetric and titration techniques represent a strategic tool. In addition, these can be considered sustainable practices in the spirit of green chemistry, avoiding high volumes of reagent wastes and enabling time- and cost-efficient research. Meanwhile, the accuracy in identifying and quantifying reactive oxidants, directly or indirectly, can be enhanced through the combination with modern instrumental exploration (electron spin resonance spectroscopy (ESR) and high-performance liquid chromatography (HPLC) or mass spectroscopy) [30,35,36] and scavenging techniques, despite being usually time-consuming and expensive. The scavenging technique is related to the use of radical scavengers, which react with the target radical oxidizing species, for selective trapping [30,35,47] during EO. The reaction between the scavenger and the radical oxidizing species decelerates the degradation of the organic pollutant investigated when EO of organic molecules is carried out in concomitance with the identification [48,49]. Another option consists in the use of the scavenging technique when electrolyzing solutions containing the oxidants precursors in absence of organics, which offers a general perspective about the production of oxidants. The $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, carbonate radical ($\text{CO}_3^{\bullet-}$), superoxide ($\text{O}_2^{\bullet-}$) ion and singlet oxygen ($^1\text{O}_2$) are identified by ESR using suitable probe molecule (e.g., 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)) registering their characteristic signals. DMPO is an excellent scavenger for $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ and $\text{O}_2^{\bullet-}$, recording defined signals like $\text{DMPO}^{\bullet}\text{-OH}$, $\text{DMPO}^{\bullet}\text{-SO}_4$ and $\text{DMPO}^{\bullet}\text{-O}_2$, respectively. Note that $\text{CO}_3^{\bullet-}$ recording defined signals like radical is a surrogate of $\bullet\text{OH}$, thus identified as $\text{DMPO}^{\bullet}\text{-OH}$ [30,46,49–51].

Meanwhile, $^1\text{O}_2$ is appointed by using TEMPO, obtaining its correspondent signal as $\text{TEMPO-}^1\text{O}_2$ in the ESR spectra. Typical ESR spectra of different reactive species are depicted in Fig. 2a [46].

Organic molecules such as DMPO, salicylic acid or *N,N*-dimethyl-*p*-nitrosoaniline (RNO) have been used to trap $\bullet\text{OH}$ by the formation of organic adducts that can be identified and quantified by HPLC (Figs. 2c and 2d) [30,46].

Following the above oxidants identification/quantification criteria in the last years, it was possible to understand that the EO has become an important process in the 21st century for electrosynthetic and environmentally friendly applications, achieving substantial advantages and

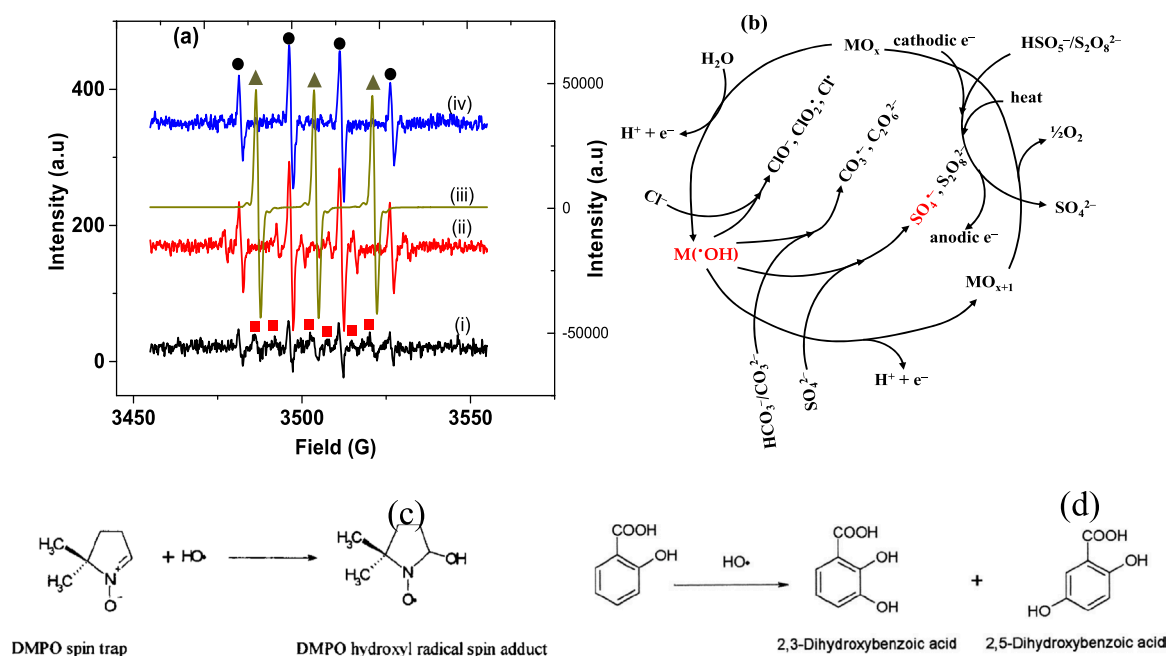


Fig. 2. (a) ESR spectra: EO with BDD anode in sulfate medium ($\bullet\text{OH}$ and SO_4^{\bullet} signals) (spectrum i); EO with BDD in real matrix containing sulfate, chloride and carbonate ($\bullet\text{OH}$ and SO_4^{\bullet} signals) (ii); spectrum of $^1\text{O}_2$ obtained during electrochemical persulfate oxidation (iii); and EO with BDD in carbonate medium ($\bullet\text{OH}$ signals) (iv). Copyright Elsevier B.V. 2020. (b) Scheme of the mechanisms of reactive species formation in EO in different media. Copyright Elsevier B.V. 2021. (c) DMPO and (d) salicylic acid as trapping agents for free $\bullet\text{OH}$.

(a) Adapted with permission from [46]. (b) Adapted with permission from [30]. (c) Adapted with permission from [18]. Copyright Electrochemical Society Inc. 2003.

solving some drawbacks related to the oxidants produced (for example, Fig. 2b) [29,30]. This investigation emerges as an extremely powerful tool in the exploration and optimization of new heterogeneous and homogenous catalytic reactions for surface-layer-based and volume-chemical-based electrochemical technologies (such as hybrid and sequential processes like EO with electrogenerated H_2O_2 , sonoelectrolysis, peroxi-coagulation, Fenton-based treatments, photoassisted electrochemical methods and so on). The advances on the mechanisms described here accelerate and simplify the investigation and optimization of new electrochemical devices over a resource-efficient scale and thus, they contribute significantly to establish the operation conditions (e.g., composition of water matrices (synthetic or actual) and electrode materials, among others).

2.2. Materials: fundamentals, the innovations on electrocatalytic anodes and future perspectives

2.2.1. Understanding the influence of the electrochemical double layer on heterogeneous electrochemical reactions

EO essentially occurs on the electrode/solution interface, therefore, the simplified scheme proposed by Comninellis [5,18] (Fig. S1) and its further extensions (see subsection 3.1) only provided general information about the oxidation pathways that could be followed by the species involved, mainly $\bullet\text{OH}$. The electrocatalytic materials used play a crucial role, which directly concerns the efficiency, selectivity and energy of the electrolytic approach, alongside other additional operation conditions [11]. From these considerations, the relevance of various aspects of the electrical double layer as for the activity and selectivity of heterogeneous (or homogeneous) electrochemical reactions remains poorly understood because of the incorrect use of Comninellis' model representations or adaptations, as indicated in the previous subsection. Particularly important are the interface dimensions and the active region in which the oxidants are formed and react. Hence, understanding the mechanisms on the electrode surface, as well as in the Nernst layer and close to it [52–54], allows the comprehension of the generation of oxidizing species and their reactivity. This is crucial to identify the

degradation byproducts and propose reaction pathways during the treatment of organic pollutants, as well as to develop specific electrochemical devices.

Typically, the structure of the electrochemical interface is constituted by (Fig. 3) [52]:

- i) the electrode, where the electrical potential or I_{appl} is controlled;
- ii) the Helmholtz plane, which is divided into the inner and outer Helmholtz planes. The former plane includes the adsorbed species on the electrode surface (i.e., solvent molecules, target pollutant and byproducts, as well as any other specifically adsorbed molecule or ion). Meanwhile, the nearest layer of ions and corresponding solvation shell are included in the outer plane, where the species are often considered as non-specifically adsorbed ions (i.e., the interaction with the surface is via electrostatic forces). This point is directly associated to the formation and the stability of the physisorbed “active oxygen” (adsorbed $\bullet\text{OH}$) and chemisorbed “active oxygen” (oxygen in the oxide

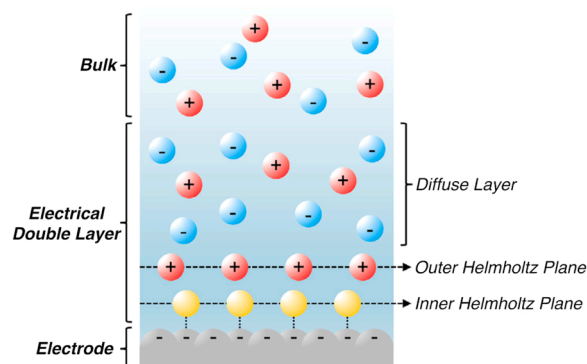


Fig. 3. Scheme of the electrical double layer. Adapted with permission from [52]. Copyright Elsevier B.V. 2018.

lattice). Consequently, the understanding of the behavior of each electrocatalytic material has been partially revealed. However, these fundamental behaviors have not been widely studied in the case of all oxidizing species in order to unveil the mechanisms to generate, decompose and activate them or to degrade organics;

- iii) the Nernst layer or diffusion layer consists of loosely alternating layers of anions and cations that maintain the charge neutrality throughout the double layer, accounting for the exponential decay of the potential away from the electrode, and
- iv) the bulk, which is the region where the electrolyte structure is no longer affected by the electrode potential.

These important considerations have allowed to clearly understand the mechanisms, representing the reaction pathways in a correct manner that allows understanding the importance of the nature of the anodic material. An excellent example is the scheme reported by McBeath and co-workers [54], which illustrates the realistic conditions and dimensions in the EO approach considering the structure of the electrochemical interface (Fig. 4). This is in contrast to other schemes that have created different controversies. Moreover, substantial developments have been achieved simulating the interactions between the species in solution (adsorbed and non-adsorbed) and the electrode surface by using theoretical and computational resources [52,53].

As stated by several experts [1,20–24,55–61], EO advantages such as high efficiency, mild operation conditions, ease of automation, versatility, and low cost (when powered by renewable energies sources [62]), have been proven by treating a wide variety of synthetic effluents or actual wastewater containing a diversity of dissolved organic compounds, achieving different results, under appropriate conditions. Nevertheless, as pointed in our previous authoritative review [1], several undefined aspects still remain to be solved to translate the technological achievements from lab to real applications, at various scales. The main parameters to be controlled are [1,61]:

- i) the electrode potential or I_{app} , which affect the current efficiencies (modest or lower to degrade organics/waterborne agents or to electrogenerated oxidants) and current or potential distribution (reactant consumption or conversion),

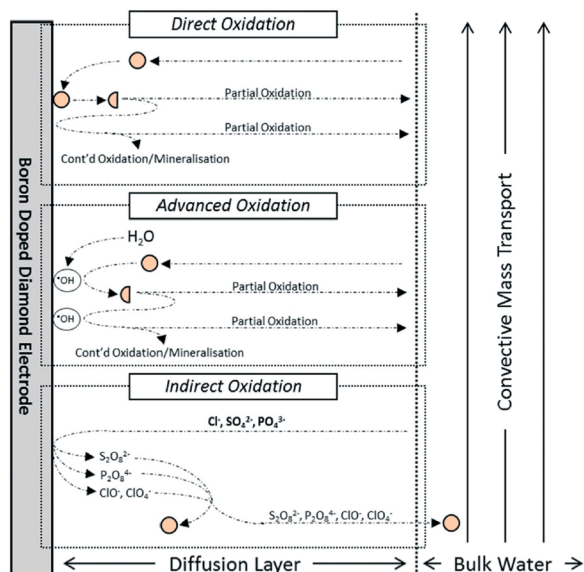


Fig. 4. Possible mechanisms for the organic contaminant degradation and mineralization during EO with BDD: Direct electron transfer, advanced oxidation and indirect oxidation.

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- ii) the electrochemical cell design (surface area to volume ratio, dimensions, turbulence promoters, electrode distance, geometry of the electrodes), which directly influences the mass transport regime (space-time yield, residence time, operation mode and uniformity of pollutants concentration in the reaction layer near to the electrode surface). Note that two cell configurations can be employed: in an undivided cell, the anodes and cathodes are in contact with the same solution without any barrier in between, whereas in a divided one, the anodes are immersed in the so-called anolyte and the cathodes in the catholyte, being both solutions connected by a salt bridge or a membrane to ensure ion transport,
- iii) the degradation/current efficiencies (operating parameters that affect the figures of merit of electrochemical treatment),
- iv) the gradient temperatures management,
- v) the pH conditions,
- vi) the pollutant type and concentration,
- vii) the effluent conductivity,
- viii) the electrode materials (preparation methods and characterization procedures) and,
- ix) the water matrices effects, as well as the occurrence of undesired reactions on the process performance.

Nevertheless, most papers devoted to the EO applicability have presented an experimental investigation in successive steps, exploring different single operation variables. Next subsections give an overview on all innovations, which are essential to understand the potential application of EO.

2.2.2. Advances on electrocatalytic materials, preparation procedures and their performance in EO

As already summarized and discussed in several reviews and books [1,15,22,24,45,56,60], the anode material is a crucial factor, in combination with other operation parameters, because it determines the abatement effectiveness, current efficiency (CE) and type of treatment (i.e., it determines the chemical and electrochemical mechanisms involved, see subsection 2.1). In fact, the selection of electrocatalytic materials regulates the direct or indirect oxidation approaches due to the ability to produce reactive oxidizing species. Fig. 5 shows the main anode materials typically used for EO [63], according to their O_2 evolution overpotential and their capacity to produce $\bullet OH$. Worth reminding, other oxidants can be chemically/electrochemically produced with those anodes, depending on the water matrices composition, as previously explained (Fig. 2b).

A huge number of electrodes (active and non-active anodes, as illustrated in Fig. 5 and Table S1) has been tested for degrading and

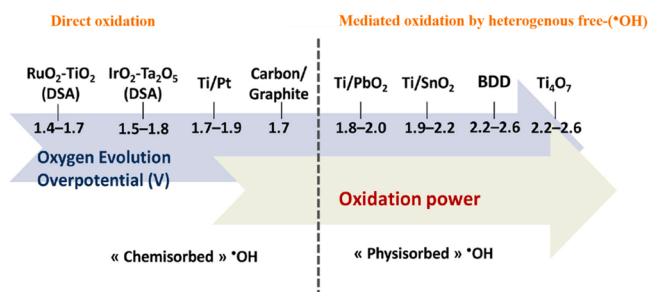


Fig. 5. Classification of the electrode materials used in EO. Non-active anodes include PbO₂, SnO₂, BDD or TiO₂, whereas mixed-metal oxides (MMO) or dimensionally stable anodes (DSA), noble metals (Pb, Au, Pt,) or some metal oxides like PtO_x as well as carbon and graphite electrodes are considered as active anodes. Direct electron transfer reactions in the potential region of water stability, whereas a relatively large overpotential for O_2 evolution in acidic media enables the production of hydroxyl radicals during water discharge. Adapted with permission from [63]. Copyright Taylor & Francis. 2020.

mineralizing a variety of organics in different water matrices (synthetic or actual) [16,22,45,63], being the so-called “non-active anodes” like PbO_2 and BDD highly effective in EO process. Nevertheless, the general rule that associates the $\text{M}(\bullet\text{OH})$ interactions, oxygen evolution and anode reactivity for organic molecules oxidation is not always obeyed because of the mixed behavior exhibited by some electrocatalytic materials, being possible to achieve comparable degradation/mineralization efficiencies with active and non-active anodes. These observations have allowed understanding that not only one type of anode or a family of anodes is appropriate for the electrochemical treatment of any effluent; instead, each one of the water matrices could be decontaminated by different electrocatalytic materials in combination with specific operation conditions. The main influence of the anode in EO derives

from the preparation method, which affects the service life, stability, electrochemical activity and selectivity.

2.2.2.1. Active anodes: MMO. Remarkable development of anode and cathode (see subsection 4) materials has been made in recent years. In particular, novel synthetic approaches have appeared to prepare active anodes. On the one hand, deposition strategies, which included the conventional thermal decomposition (e.g., sol-gel and Pechini) and electrodeposition, as well as heating methods based on microwaves and laser sources have been successfully improved or recently developed [15,58]. On the other hand, novel solvents such as ionic liquids (ILs), deep eutectic solvent (DES) and polyvinyl alcohols (PVA) were used to

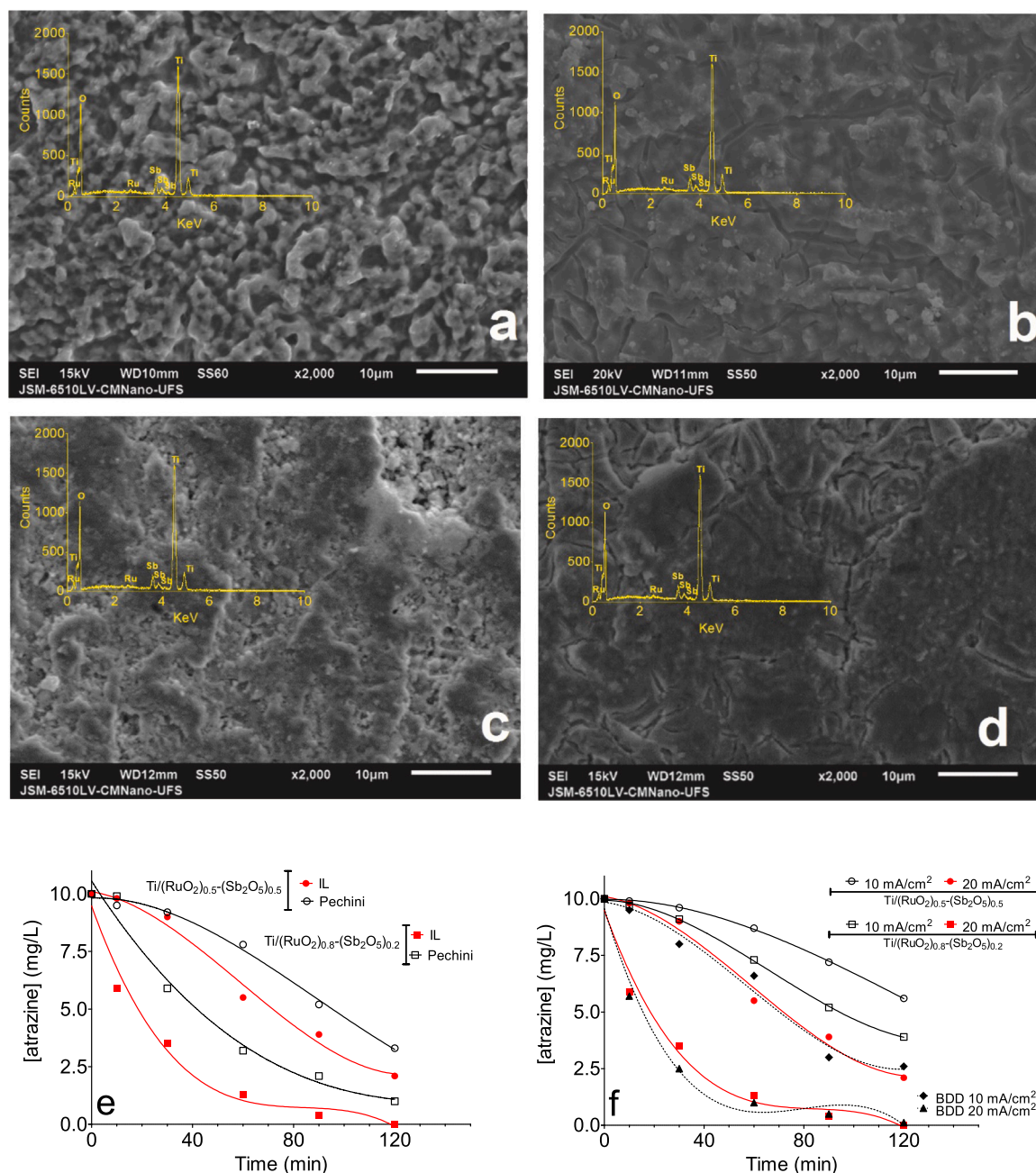


Fig. 6. SEM images (at 2000 ×) with EDX analysis for: (a, b) $\text{Ti}/(\text{RuO}_2)_{0.5}-\text{(Sb}_2\text{O}_5)_{0.5}$; (c, d) $\text{Ti}/(\text{RuO}_2)_{0.8}-\text{(Sb}_2\text{O}_5)_{0.2}$. Both anodes were synthesized (a, c) in ILs at 600 °C and (b, d) by Pechini method at 400 °C. Insets: EDX analysis for each DSA. (e) Effect of synthesis method during the EO of atrazine at 20 mA cm⁻². (f) Comparison of elimination performances achieved with DSA synthesized in ILs and BDD anodes, at different I_{appl} . Solutions: 40 mL of 0.1 M Na_2SO_4 containing 10 mg L⁻¹ atrazine at 25 °C.

Adapted with permission from [67]. Copyright American Chemical Society Inc. 2000.

modify the support by thermal or electrodeposition methods to form and add the electrocatalytic film.

RuO_2 is the most used metal oxide among active anode materials due to its electrocatalytic activity, even when corrosion phenomena in electrolytic acidic conditions have been demonstrated, affecting its stability upon long-term use [64]. Using Sb_2O_5 , IrO_2 or TiO_2 as stabilizers, its stability has been enhanced. In the case of ILs solvent strategy, the optimization of new electrode synthesis steps on a resource-efficient scale enables a time- and cost-efficient research [65]. For example, two types of ILs to produce a $\text{Ti}/(\text{RuO}_2)_{0.8}\text{-(Sb}_2\text{O}_5)_{0.2}$ anode were recently investigated by Santos et al. [65], concluding that 2-hydroxyethylammonium acetate solvent provides higher stability, higher voltammetric charge and high electrocatalytic activity to the anode, while lower charge transfer resistance was also achieved. Thus, these catalytic features allowed treating a synthetic effluent with Reactive Yellow 186 (100 mg L^{-1}) by applying 10 mA cm^{-2} to an anode of 2 cm^2 immersed in 100 mL of $100 \text{ mM Na}_2\text{SO}_4 + 10 \text{ mM NaCl}$, achieving 100% TOC removal in 120 min. Using a $\text{Ti}/\text{RuO}_2\text{-IrO}_2$ anode, a high stability was achieved when it was prepared using PVA as a solvent [66]. This feature was more evident when 0.1 L of a synthetic solution of Reactive Blue 21 (50 mg L^{-1}) were electrolyzed in NaCl (ranging from 0.1 to 20 M) applying 25 mA cm^{-2} because the PVA-made anode was more effective to eliminate the dissolved organic matter (100% TOC removal in 30 min), increasing the kinetic rate constants by 2-fold as compared to the Pechini-made anode. Interestingly, an unexpected enhancement of the electrocatalytic nature of DSA electrodes was achieved by ILs method (including the thermal decomposition step) compared to similar electrodes obtained by Pechini approach and BDD anode [67]. SEM analysis revealed that films were homogeneously deposited in the case of anodes made in ILs ($\text{Ti}/(\text{RuO}_2)_{0.5}\text{-(Sb}_2\text{O}_5)_{0.5}$ and $\text{Ti}/(\text{RuO}_2)_{0.8}\text{-(Sb}_2\text{O}_5)_{0.2}$), and no typical DSA-crack morphology was observed, in contrast to that coatings obtained by the Pechini method (Fig. 6). The parameters evaluated through electrochemical characterization (resistance, surface area and roughness) were significantly improved as compared to those determined for the Pechini-made electrodes, which was attributed to the grainy surface obtained by the ILs-thermal decomposition procedure [67]. Using both ILs-made anodes for atrazine (10 mg L^{-1}) degradation for 120 min in 40 mL of $0.1 \text{ M Na}_2\text{SO}_4$ at 25°C , the herbicide was efficiently eliminated. By applying 20 mA cm^{-2} , 79% and 100% of atrazine was removed with $\text{Ti}/(\text{RuO}_2)_{0.5}\text{-(Sb}_2\text{O}_5)_{0.5}$ and $\text{Ti}/(\text{RuO}_2)_{0.8}\text{-(Sb}_2\text{O}_5)_{0.2}$, respectively, as shown in Fig. 6e. These electrodes improved the degradation removals achieved at Pechini-made DSA anodes (67% and 90% of atrazine elimination using $\text{Ti}/(\text{RuO}_2)_{0.5}\text{-(Sb}_2\text{O}_5)_{0.5}$ and $\text{Ti}/(\text{RuO}_2)_{0.8}\text{-(Sb}_2\text{O}_5)_{0.2}$, respectively, Fig. 6e). Comparing the performances with a non-active anode like BDD, $\text{Ti}/(\text{RuO}_2)_{0.8}\text{-(Sb}_2\text{O}_5)_{0.2}$ behaved similarly to remove atrazine (98% in 100 min). TOC removal percentages of 90% and 95%, and COD removal percentages of $\approx 93\%$ and $\approx 97\%$ were achieved using $\text{Ti}/(\text{RuO}_2)_{0.8}\text{-(Sb}_2\text{O}_5)_{0.2}$ and BDD, respectively, at 20 mA cm^{-2} , clearly evidencing an important enhancement of the electrocatalytic activity of ILs-made anode. This was explained by the possible homogeneous distribution of active sites of Ru that favored the efficient production of oxidizing species like free heterogeneous $\bullet\text{OH}$. This result clearly evidenced that novel methods can significantly contribute to control and improve the characteristics of the metal oxide coatings (Fig. 6 f), developing anodes that could have comparable EO performance to diamond films. This is a remarkable result, since it allows scaling-up the EO technology from small devices to pre-pilot industrial treatment plants with more affordable anodes (in terms of durability, efficiency and cost). Alternatively, Gonzaga et al. [68] developed a hybrid microwave/conventional heating system to synthesize $\text{Ti}/\text{RuO}_2\text{-IrO}_2$ anodes where changes in the heating procedure were adopted during the thermal decomposition method, resulting in an important enhancement on the electrode surface morphology because the service life was extended to approximately 15 years (which was estimated by durability tests under extreme experimental conditions), as well as

improvements on the mineralization performance for the indirect EO when Methylene Blue (50 mg L^{-1}) was treated in NaCl medium at 25 mA cm^{-2} , reaching 100% of color and 64% of TOC removals in 60 min

A novel heating method was recently reported by using a CO_2 laser to prepare $\text{Ti}/\text{RuO}_2\text{-TiO}_2$ anodes [69,70], improving its electrocatalytic activity due to an expansion on its surface area and, consequently, increasing the amount of active sites that participated in the electro-generation of reactive oxidizing species like active chlorine and free heterogeneous $\bullet\text{OH}$.

In fact, electrochemical treatment of clopyralid pesticide was possible by electrolysis, photoelectrolysis [70,71] and EF [72] thanks to the electrochemical and photoactive features presented by the laser heating-prepared anode. The results obtained at lab scale were subsequently used to design and construct a microfluidic flow reactor, expanding the dimensions of the $\text{Ti}/\text{RuO}_2\text{-TiO}_2$ laser-prepared anode [71], indicating that this innovative preparation procedure is a potential tool to obtain stable and scalable materials for water and wastewater treatment. Actually, a limited number of studies have dedicated efforts to the MMO scale up to demonstrate their successful application on a large scale [73]. However, the nanotechnology could be an interesting alternative for modifying supports or create novel nanostructured surfaces [74].

Conversely, the advantages of electrodeposition (i.e., easy adjustment of experimental conditions, quick deposition and good cost-benefit balance) have drawn great attention to efficiently prepare different anode materials [75] that increase their catalytic efficiency in the EO of organics. An example is the modification of DSA with Pt to be used in the electrochemical degradation of 0.1 L tetracycline hydrochloride [75] (0.45 mM) in $0.1 \text{ M H}_2\text{SO}_4$ at 100 mA cm^{-2} . Concentration removal about 97.2% in 180 min under optimal conditions was achieved. This intensification on the removal efficiency was directly associated with the increase on the active electrochemical area of the Pt-electrodeposition-modified anode. In the case of non-active anodes, which produce efficiently and large amounts of the free heterogeneous $\bullet\text{OH}$, the research about novel synthesis methods has examined how to reduce/eradicate their most important drawbacks (such as short service life and large coating corrosion, provoking hazardous ions contamination [76]). In this context, Sn- and Pb- based oxides have received great attention because of their high oxidation performance, stability and low cost. Modified-synthesis strategies have been developed, with the use of dopants or interlayers, and the elaboration of novel substrates, among others [58,74].

Discarded SiC heating rods, as stable substrates, were used to prepare SiC/Sb-SnO₂ anodes; nonetheless, ILs [77] and DES [78] were strategically utilized as solvent precursors to synthesize SnO₂-Sb-Ce, SnO₂-Sb-Ta, SnO₂-Sb-Bi and SnO₂-Sb-Gd, as well as Ti/SnO₂-Sb electrodes, respectively. In all cases, the service lifetime and EO performance were enhanced as compared to the conventional Sb-based oxides. Regarding the expansions on the substrates in order to increase the stability or the electrochemical activity of the SnO₂ films, TiO₂ nanotubes have gained great interest among the environmental electrochemists. In fact, TiO₂ nanotubes implanted with g-C₃N₄ nanosheets [79], TiO₂-nanotubes/SnO₂-Sb [80] with carbon aerogels, and Sb-SnO₂/IrTaO_x/TiO₂-nanotubes [81] have been synthesized and tested for removing catechol (100 mg L^{-1}), tetracycline (100 mg L^{-1}) and 4-chlorophenol ($400 \mu\text{M}$), achieving removals of about 98%, 100% and 100% in terms of the pollutant concentration, respectively. Solutions of 80 mL of Methylene Blue (20 mg L^{-1}) in $0.1 \text{ M Na}_2\text{SO}_4 + 0.02 \text{ M NaCl}$ were electrochemically treated with a laser heating-made Ti/SnO₂-Sb anode (2 cm^2) at 40 mA cm^{-2} , obtaining higher removals in short time (100% of the dye removal after 15 min) when compared to the conventionally made anodes with the same composition [69]. Other electrocatalytic materials have been also prepared by magnetic particles immobilization in order to obtain hybrid electrodes. For example, 2.5D Ti/Sb-SnO₂/polyaniline [82] and Ti/IrO₂-Ta₂O₅ loaded by

$\text{Fe}_3\text{O}_4/\text{Sb-SnO}_2$ particles [83]. These methodologies led to enhancements on the lifetime of the coating and oxidation abilities to produce oxidizing species, which promote the elimination of organics, like Acid Red G [82,83] and phenol [83] from synthetic effluents. When removing color of Acid Red G solutions, higher removal efficiencies were achieved using $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ loaded with $\text{Fe}_3\text{O}_4/\text{Sb-SnO}_2$ particles as compared to 2D $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ and 2D $\text{Ti}/\text{Sb-SnO}_2$, respectively [83]. The superiority was also demonstrated by degrading phenol. In both cases, a synergistic effect was attained between $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ and magnetic Sb-SnO_2 particles, improving the electrocatalytic properties of this type of electrodes. A non-active/active character was conferred and, consequently, it allowed the co-existence of direct and indirect EO approaches.

2.2.2.2. Non-active anodes: lead oxide. Lead oxide-based anodes are also considered non-active anodes in EO, similarly to SnO_2 , Ti_4O_7 and BDD anodes, since no catalytic active sites are provided to favor direct anodic reactions or adsorption of byproducts on their surfaces [1,56,76]; however, as previously exposed, lead oxide-based electrodes may suffer from corrosion, releasing Pb^{2+} ions in solution and, consequently, limiting their applicability in water treatment. Nevertheless, the stability of these electrodes has been increased by novel preparation strategies. PbO_2 -decorated Co_3O_4 nanowire (NW) arrays [84], 2.5D $\text{PbO}_2/\text{Sb-SnO}_2$ [85], 2.5D $\text{PbO}_2/\text{Pb}_3\text{O}_4$ [86] magnetically assembled electrodes and carbon black (CB) modified- PbO_2 (CB- PbO_2) [87] showed relevant stability and electrocatalytic properties. In the former, service life was significantly increased in some cases, while the ability to produce free heterogeneous $\cdot\text{OH}$ was considerably improved in all cases, in the latter, attaining higher removal efficiencies when compared with their counterparts (such as Ti/PbO_2 or Pb/PbO_2).

TiO_2 -nanotubes decorated with PbO_2 supported on Ti (Ti/TiO_2 -nanotubes/ PbO_2) were tested as anodes to degrade Methyl Red (25 mg L^{-1}) dye solution (in $0.5\text{ M H}_2\text{SO}_4$) at 30 mA cm^{-2} with magnetic stirring by EO and photoelectrocatalytic (PEC) processes, achieving 100% of concentration removal after 110 and 35 min, respectively. Although higher removal efficiency was achieved by PEC method, which demonstrated a synergistic effect produced by the combination of TiO_2 and PbO_2 in a nanostructured array, the use of this preparation approach provided more stability for this type of non-active anode [88]. Previous results allowed obtaining large disk electrodes of Ti/TiO_2 -nanotubes/ PbO_2 (65 cm^2) by anodization and electrodeposition procedures [89,90]. They were used in an electrochemical flow cell to electrochemically treat 1.0 L of solution containing 250 mg dm^{-3} of the textile dye Acid Blue 113 (AB113) using Na_2SO_4 as supporting electrolyte, applying 20, 40 and 60 mA cm^{-2} [89]. This is an investigation that evidenced the feasibility to increase the electrode dimensions for industrial EO applications. The results showed that the AB113 was efficiently eliminated from synthetic effluent via free heterogeneous $\cdot\text{OH}$ at Ti/TiO_2 -nanotubes/ PbO_2 electrode when compared with Ti/Pt and Pb/PbO_2 , providing higher oxidation rates, higher current efficiencies and lower energy requirements than the other electrodes (Ti/Pt and Pb/PbO_2). The Ti/TiO_2 -nanotubes/ PbO_2 service life was also significantly extended and no pollution by Pb^{2+} ions was observed during its use in EO experiments [90].

2.2.2.3. Non-active anodes: diamond. The most remarkable EO results have been achieved with diamond films and Ti_4O_7 [1,8,22,26,42,91–101]. Diamond electrodes are considered the best non-active anodes in EO due to their great effectiveness to mineralize different organic pollutants in wastewater treatment by free heterogeneous $\cdot\text{OH}$. Therefore, it seems interesting to modify the diamond film preparation, employing different supports (W, Ta, Nb, Si, Ti) [42,102,103], modifying their surfaces (including nanostructures [104–106] and nanoparticles [74], varying the sp^3/sp^2 relationship [42,107–115], the boron-doping level [116] or the diamond size-grains/crystals [117], and

even making porous diamond films). Examples of diamond-carbon nanostructures are shown in Fig. 7. Synthetic diamond films can be synthesized by high pressure high temperature (HPHT) and chemical vapor deposition (CVD) techniques [36,102] with different structural characteristics (size of the diamond crystals, such as microcrystalline diamond (MCD), nanocrystalline diamond (NCD) and ultra-nanocrystalline diamond (UNCDD)) onto diverse substrate materials (e.g., Ti, Si, W, Mo, Nb, Pt and carbon) [102].

Deposition of high-quality diamond depends on the procedure, reactor design and proper reaction conditions, which can influence their main properties (low capacitance, featureless background current, large signal to noise ratio and chemical stability as well as the nucleation rate of diamond grain, then the growth rate and quality during the deposition) [36,103]. In EO and other electrochemical technologies applied to water disinfection or wastewater treatment, MCD is mainly used (showing grain size larger than $1\text{ }\mu\text{m}$ with large roughness) [102]. Meanwhile, NCD and UNCDD coatings are typically used for electroanalysis and sensors, including their application in environmental directions. A diamond surface controlled-doping level with boron, nitrogen, fluorine, phosphorous or sulfur must be performed to provide adequate electrical conductivity. Boron doping has been preferred to the other ones, demonstrating that average optimal boron concentration is approximately $3 \times 10^{20}\text{ atoms cm}^{-3}$, becoming BDD an interesting electrocatalytic material for EO, electroanalysis, electrosynthesis and energy conversion investigations [36,102,118]. Based on the intense investigations in the last years, BDD electrochemical properties are impacted/affected by the surface termination, sp^3/sp^2 ratio, surface defects, B content, crystal size and morphology roughness of diamond films [36,42,102]. Nevertheless, the sp^3/sp^2 relationship and boron doping level have received great attention because the former strongly modifies the adsorption character, owing to the relaxation of the grains on diamond surface, whereas the latter affects the sp^2 distribution at grain boundaries [42,110–113,116,119], influencing the production of reactive oxidizing species. For this reason, a higher sp^3/sp^2 ratio is ideal to avoid the generation of hazardous species [26], while it favors the complete mineralization of organic pollutants [107,115,120]. In fact, Gomez-Ruiz and co-workers [121] recently revealed that higher sp^3 carbon content, lower boron and H-terminated carbon content of the MCD favored a faster and more efficient perfluorooctanoic acid degradation than UNCDD. This behavior can be a result of the higher production of free heterogeneous $\cdot\text{OH}$ or persulfate under specific conditions [111–113,119]. The study of sp^3/sp^2 relationship was a parameter also investigated on BDD surface as cathodic material during the electroreduction of CO_2 , demonstrating that higher electrochemical conversions to carboxylic acids can be achieved [122–125] and, consequently, evidencing that it plays a key role in anodic or cathodic EO transformations.

2.2.2.4. Non-active anodes: titanium suboxide. In the case of the Ti_4O_7 , a similar EO performance to that of BDD has been demonstrated to eliminate some organics from wastewater. This material is a Magnéli phase of titanium suboxide that can electrochemically produce weakly adsorbed hydroxyl radicals from water discharge and other oxidizing species under specific conditions [92,93,97,100,126]. At the same time, it has been evidenced that it is sufficiently stable under aggressive experimental conditions and it is not as fragile as Si/BDD , allowing its use in small electrochemical reactors or pilot plants. Recently, dyes and perfluoroalkyl substances have been electrochemically treated with Ti_4O_7 anodes [127,128], which were prepared by spark plasma or high-temperature sintering methods, achieving higher removal efficiencies and higher oxidation rates than those achieved with the commercial DSA anodes. On the other hand, EO experiments with feed concentrations of either oxalic acid (1 mM) or terephthalic acid (0.1 mM) were carried out in 100 mL of a solution of 0.1 M NaClO_4 as supporting electrolyte [94], achieving the oxidation of oxalic acid by

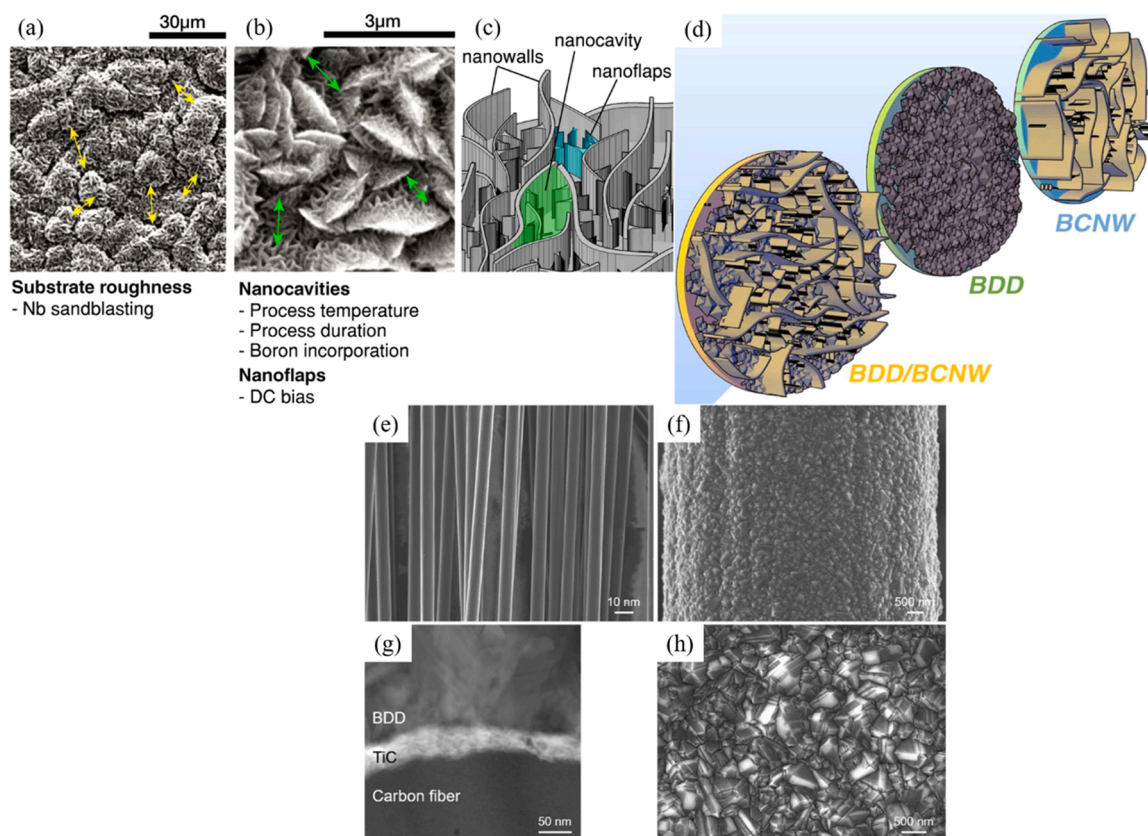


Fig. 7. (a, b) SEM images of the carbon nanoarchitecture comprising boron-doped vertically aligned graphene walls (BCNW) that were grown on a BDD interfacial layer deposited on Nb. (c) Schematic representation of the BCNW morphology. (d) BDD/BCNW assembly. Diamond fibers (DFs): (e, f) FESEM images in the secondary electron mode; (g) dark field STEM image; (h) FESEM image of the used planar BDD film.

(a-d) Adapted with permission from [104]. Copyright Elsevier B.V. 2021. (e-h) Adapted with permission from [117]. Copyright Elsevier B.V. 2021.

direct electron transfer or mediated free heterogeneous $\bullet\text{OH}$ depending on the electrical potential applied (anodic potentials of 2.66 and 3.16 V|SHE, respectively). Meanwhile, terephthalic acid was used as a probe molecule that is resistant to direct electron transfer reactions and readily reacts with $\bullet\text{OH}$, decaying terephthalic acid concentration at 2.86 V|SHE. The formation of 2-hydroxyterephthalic acid was used to evaluate the relative $\bullet\text{OH}$ production and lower restrictions on steady state $\bullet\text{OH}$ concentrations. In practice, Oturan's group has evidenced that sub-stoichiometric Ti_4O_7 ceramic electrode could be considered as a feasible alternative to BDD, in terms of cost, stability and pollutants oxidation [92,93]. The oxidation efficiency of Ti_4O_7 was already compared with different anode materials, i.e., DSA, Pt and BDD, for EAOPs like EF and $\text{EO-H}_2\text{O}_2$ to eliminate the anti-cancer drug imatinib from water, finding that the oxidation/mineralization power of different anodes was ranked as $\text{BDD} \geq \text{Ti}_4\text{O}_7 > \text{Pt} > \text{DSA}$ [129].

As mentioned above, an extensive variety of organic model compounds have been treated by EO approach with several anodes, including diamond electrodes [95,130], which have achieved higher removal and higher current efficiencies than other. During the last years, many papers have published investigations related to the use of diamond films on EAOPs for the abatement of target organic pollutants such as dyes, phenolic compounds, carboxylic acids, pesticides, herbicides, surfactants, drugs, pharmaceuticals, pigments [36,131–134], and waterborne agents [26], giving broad information related to the operation conditions, diamond films quality, EO performance, surface and bulk behaviors, advantages, disadvantages, oxidizing species produced, hybrid and combined diamond EO technologies, electrochemical reactors, and so on. These facts have allowed to solve few limitations of diamond electrodes for their industrial applications as well as to eradicate some misunderstandings. On the one hand, the most recent uses are

related to the electrochemical treatment of real wastewater or different water matrices, allowing understanding the following aspects:

- sometimes, the diamond-based electrolytic technologies accomplish efficiently the waters decontamination, but sometimes not,
- when a partial elimination of the pollutants is achieved, a combination of technologies is recommended,
- the cost and electrode dimensions are hypothetical disadvantages because small-diamond electrochemical devices can be constructed to specific applications.

On the other hand, it is necessary understand the following aspects:

- diamond electrodes are not completely ideal non-active anodes due to their surface features; as explained above, they also promote direct oxidation by active sites, and they could be currently considered as a "versatile electrode",
- not only free heterogeneous $\bullet\text{OH}$ are produced; other oxidants can also be generated via the participation of $\bullet\text{OH}$ or not (for example, persulfate can be electrogenerated from diluted sulfate solutions),
- the oxidation via free heterogeneous $\bullet\text{OH}$ occurs as a surface-layer phenomenon inside the reaction cage (i.e., Nernst layer and close to it) [28], mainly due to the extinction time of the $\bullet\text{OH}$, and
- toxic byproducts species can be avoided or their production can be controlled.

From a critical point of view, nowadays, the application of EO using BDD anodes to industrial- and domestic-scale water decontamination,

including wastewater treatment and water disinfection, can be considered the main scientific contribution [26,36,131–134]. Selected examples are exposed in Table S1. At the same time, more efforts have been dedicated to obtain BDD electrodes in different formats (2D or 3D arrangements), dimensions (from cm^2 to m^2) and with significant surface properties, facilitating that more research groups develop their own home-built systems. More commercial companies have appeared in the sector of the diamond films (Condias or Diachem® (Germany), CSEM (Switzerland), Advanced Diamond Technology (USA), METAKEM (Germany), Element Six (Luxembourg), NeoCoat (Switzerland), Water-Diam (France)) [36]. In this regard, thanks to the scientific advances and collaboration between universities/research institutions and companies via technology transfer, more diamond-electrochemical devices are being designed and constructed, allowing the upgrading from initial Technology Readiness Level (TRL) to mature technologies in specific operations, as discussed in the last section of this critical review.

2.2.2.5. Innovative anodes. Regarding the innovative insights related to the real water matrices treatment and the preparation of novel electrocatalytic materials; the EO of ILs, perfluoroalkyl substances, herbicides, municipal wastewater effluents, hospital wastewater, groundwater, petrochemical effluents, wastewater from agri-food activities as well as deactivation of microorganisms for water disinfection or food control, are the most relevant so far.

For example, EO of 1-butyl-3-methylimidazolium chloride (BMImCl) was investigated by using different BDD anodes with sp^3/sp^2 ratio [107]. At a higher sp^3/sp^2 ratio, a stronger oxidation of BMImCl was promoted at 100 mA cm^{-2} , avoiding secondary species such as chlorate and perchlorate. Analyzing the noxiousness of the treated effluents, the final effluent was more toxic, suggesting that other treatments should be applied. Efficient diamond-electrochemical devices for use in specific situations could be commercialized.

Currently, perfluorinated compounds [135–139] have received great attention as micropollutants. In this regard, perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) were treated, under galvanostatic conditions at 25°C , using Ti/SnO₂-Sb-Ce, Ti/SnO₂-Sb/Ce-PbO₂, and Ti/BDD anodes [137], achieving 98.7% and 96.0% removals of PFNA and PFDA, respectively, after 180 min, when a solution of 100 mL of 0.25 mM PFNA + 10 mM NaClO₄ was electrolyzed at 10 mA cm^{-2} . EO experiments with BDD anode of solutions containing perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were also investigated [138], concluding that PFOA is quickly removed than PFOS. Meanwhile, mediated Cl^- -EO assessed $\approx 20\%$ of removal efficiencies on the defluorination rate of PFOA or PFOS.

In accordance with the literature, intensification on the electrochemical treatment of herbicides by EO approach has been observed in the last years. In this context, the greater capacity of BDD for the mineralization of herbicides when compared with the performances achieved at other non-active and active anodes has been proven by EO, as in the case of pyridine picloram (at PbO₂) [140], 2,4-D (at Pt) [141], and benzoic acid clopyralid (at Ru-Ti oxides) [142]. For example, atrazine was reduced by 30% in 0.033 mM Na₂SO₄ after 60 min of electrolysis by applying 50 mA cm^{-2} using a cylindrical two-electrode cell with a DSA of Ti/Ru_{0.3}Ti_{0.7}O₂, whereas it was electrochemically mineralized after 30 min with 0.10 M NaCl [143]. Atrazine degradation with BDD in sulfate medium was predominantly achieved by heterogeneous free-(•OH) and it may be also oxidized by persulfate participation; when chloride medium is used with DSA anode, atrazine is more rapidly removed due to the chemical volume-based oxidation approach by active chlorine species. However, when TOC removals are compared, 33% is achieved at 60 min using BDD, but only 13% with DSA in 0.033 mM Na₂SO₄, whereas in 0.10 M NaCl, an opposite effect was attained, achieving 79% for BDD and 56% with DSA, which can be due to the faster mineralization of the chloroderivatives. These non-desired byproducts from the oxidation action of active chlorine with atrazine are

efficiently eliminated by the free heterogeneous •OH produced at BDD (see also Section 3.2.3).

RuO₂-based DSA have been extensively used in the EO of herbicides, due to large stability for their application in synthetic sulfate and chloride media, as compared to BDD anodes (because of their high cost). For example, Ti/Ru_{0.3}Ti_{0.7}O₂ with chloroacetanilide alachlor [144] and 2,4-D [145], Ti/(RuO₂)_{0.8}(MO₂)_{0.2} (M = Ce, Sn or Ir) with atrazine [146], Ti/(RuO₂)_{0.5} – (Sb₂O₅)_{0.5} and Ti/(RuO₂)_{0.8} – (Sb₂O₅)_{0.2} with atrazine [147], Ti/RuO₂-IrO₂ with the urea nicosulfuron [148] and Ti/(RuO_{0.36}Ti_{0.64}O₂ with diuron [149]. PbO₂ anodes have been also used for treating picloram [140] and 2,4-D [150] with β -PbO₂, glyphosate with Ti/PbO₂ [151], the triazine metribuzin with PbO₂/WO₃ [152] and the triazine metamitron with PbO₂-CeO₂ [153]. For example, 100% of degradation and 76% of COD removal were achieved with a PbO₂/WO₃ anode for 200 mL of 40 mg L^{-1} metribuzin in 0.050 M Na₂SO₄ at pH 4.0 by applying 560 mA for 90 min. Other EO examples using BDD electrodes are for degrading glyphosate [154], 2,4-D [114] and tebuthiuron [155]. It is important to remark that a significant number of these anodes has been prepared by the novel synthetic methods discussed above; then, these electrodes constitute a more environmentally-friendly option than classical diamond films.

The possibility to electrochemically treat sanitary landfill leachates, which are considered a critical environmental problem, is a key challenge. Fernandez et al. [156,157] studied the treatment of sanitary landfill leachate using BDD anode, assessing a complete elimination of COD and dissolved organic carbon (DOC) after 8 h, as well as a total dissolved nitrogen (TDN) decay about 80%. The effectiveness of EO to reduce physical-chemical parameters and ecotoxicity of sanitary landfill leachate was also evaluated by using *Daphnia magna* as model organism, reaching a decay in the acute toxicity of approximately 59% [156]. Meanwhile, the biodegradability index (BOD₅/COD) was 0.84 because the organic matter, ammonium nitrogen and heavy metal ions (e.g.: Cd and Pb) were significantly reduced after 36 h of EO treatment. A performance comparison between Ti/BDD and Ti/RuO₂ anodes [158] in the electrolytic treatment of biological leachate was carried out, being BDD superior to DSA because higher COD and TOC removals (95% and 92%, were obtained, respectively). Meanwhile, Ti/RuO₂ efficiently removed NH₄⁺-N and total nitrogen with a maximum of 98% and 72%, respectively. Similar effluents were investigated by using diamond-carbon nanoarchitectures [104], as BDD/BCNW anode (Fig. 7), resulting in an enhancement on the COD and TOC removals as compared to the conventional planar BDD electrode. Its effectiveness was due to the higher exchange current density and an enhancement on its effective surface area. These findings inspired the preparation of a novel 3D macro-porous BDD foam electrode with a structure of evenly distributed pores and interconnected networks [159]. This interesting synthetic 3D BDD anode allowed a significant increase of its electroactive surface area (20-fold) and EO reaction rate constant (350-fold) of Reactive Blue 19 (RB-19) textile dye as compared to a planar BDD. The diamond fibers (DFs) application as nanostructure (Fig. 7) for the EO of Methyl Orange, phenol, and tetracycline was also tested [117]. The initial concentration of 100 mg L^{-1} of Methyl Orange was reduced down to 89.3% within 100 min, being superior to that reached with a planar BDD electrode. When 50 mg L^{-1} of Methyl Orange, phenol and tetracycline were electrochemically treated with DFs, complete removal was achieved at 120, 110 and 90 min, respectively.

More examples of preparation procedures, characterization methods and surface modification methodologies could be commented here. However, the objective was to expose the most relevant examples, evidencing the most important advances and developments as well as illustrating the most relevant results obtained for priority pollutants. More specific examples can be consulted in the authoritative reviews published by experts in the field [74].

It is also important to remark that, although significant progress has been achieved about the electrode preparation, the geometrical areas prepared typically ranging from 2 to 20 cm^2 as well as their EO

performances to eliminate organic pollutants from solutions have been evaluated by using batch or beaker reactors or cells with stirring, which has limited the scale-up of the electrolytic technologies. Only in a couple of examples the geometrical area of the electrocatalytic materials has been successfully increased and, consequently, these materials have been used in electrochemical flow reactors, increasing the effluent treated volume that led to a techno-economic estimation [71,90].

Another feature that must be considered is the cost and time needed for the anode preparation. In this regard, new methodologies have been investigated for improving the sensitivity, selectivity, consistency and effectiveness of traditional materials. Lately, the nanotechnology has been introduced as a hot topic, allowing a better understanding of the chemical/electrochemical processes that take place on the micro- and nano-environments. Moreover, it provides significant new benefits such as greater catalytic sites effectiveness, real-time monitoring and high sensitivity-selectivity as a consequence of the high and efficient oxidation power and mass transport phenomena. Among the various types of materials, hybrid materials have found extensive use in electrochemistry because of their desirable properties: high chemical stability, robustness, electrical conductivity and surface area, outstanding electrocatalytic activity and mixed catalytic behavior, among others.

2.2.3. Applications of computational chemistry

As commented in subsection 2.2.2, it is vital to understand the effect of the electrochemical double layer on heterogeneous electrochemical reactions; therefore, theoretical and computational chemistry have fascinatingly emerged as a powerful tool, which uses first-principles or empirical methods to predict transformation behaviors as well as the structure and the effect of several double layer properties in electrochemical systems [52,54]. In the last years, these computational methods have received great attention by the environmental electrochemistry community, especially by the research groups that have dedicated major efforts to consolidate the EO-based technologies.

Looking at the structure of water matrix/solution at the electrode-electrolyte interface (Fig. 3) [52], the electrochemical reactions are of particular importance. Nevertheless, from a microscopic point of view,

the use of instrumental analysis techniques for exploring the double layer structure in actual water matrices becomes too complex or yields unreliable results due to the presence of multiple components. This is more evident for complex matrices when pollutants (organic or inorganic), reactive oxidizing species (radical or nonradical) and natural organic matter (NOM) are present. In this context, computational approaches are attractive by using simulations, modelling, theoretical or computational calculations, in order to analyze [160,161]:

- i) the potential dependence behavior of solvents,
- ii) current-induced interfacial concentration gradients and their effect on electrochemical kinetics,
- iii) on-specifically adsorbed cations effects in the outer Helmholtz plane on reaction selectivity and activity,
- iv) the interactions between the electrode and pollutants,
- v) the effects of the electronic structure of the anode on the conformational dynamic interactions,
- vi) the multi-point interactions that could be attained between organic compound, oxidants and anodic surface,
- vii) the mechanisms of the volume-based chemical oxidation reactions like oxidants, mediators and pollutants, and
- viii) the presence of adsorbed or non-adsorbed species on the anode surface.

Recent advances in both experimental and computational methods for analyzing the aspects mentioned above have been performed in the last years. In fact, the number of scientific reports that have used the theoretical or computational procedures for interpreting/simulating/modelling/combining the experimental findings on the EAOPs has significantly increased (Fig. 8a). However, important challenges in studying the EO processes (direct or indirect), from the theoretical point of view, at the electrode-electrolyte interface still exist.

Quantum (i.e., ab initio methods) or molecular (i.e., empirical methods) mechanics calculations have been applied in electrochemistry. In the former, theoretical chemistry methods (e.g., Density Functional Theory (DFT), post-Hartree-Fock and Hartree-Fock) [160] are applied

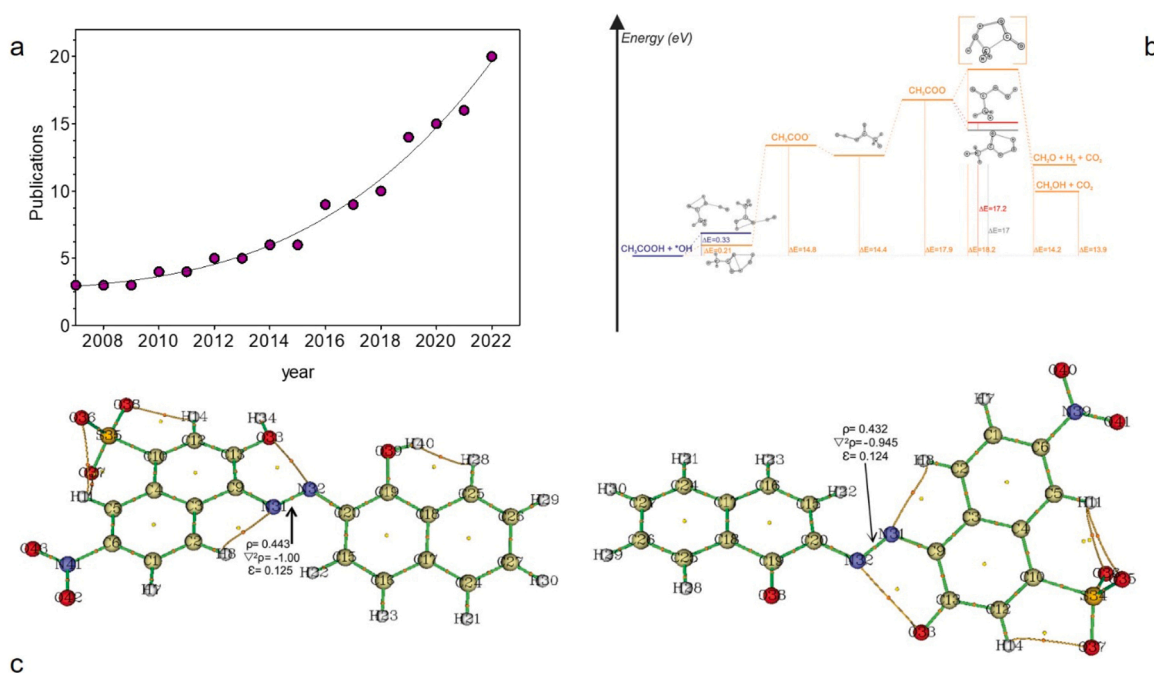


Fig. 8. (a) Number of publications on computational chemistry applied to EAOPs. (b) Potential energy surface (PES) obtained by using B3LYP/6–311 + +g(d) for interactions and possible products of the acetic acid (AA) reaction with hydroxyl radical, using Gibbs's energies. (c) Molecular graphics with critical points and values of ρ , $\nabla^2\rho$ and ϵ from Eriochrome Black T and complexes with optimized structures.

(a) Adapted with permission from [162]. Copyright Elsevier B.V. 2017. (b) Adapted with permission from [163]. Copyright Elsevier B.V. 2020.

by combining different software (e.g., Gaussian series software); examples of applications of molecular mechanics include modelling of biological systems and materials assembly with thousands to millions of atoms.

Precise or accurate predictions/descriptions of electronic properties, molecular structure and reaction mechanisms or chemical processes involving electrons (e.g., breaking or forming chemical bonds) can be provided by using quantum mechanics calculations. Therefore, this computational tool is valuable in environmental electrochemistry research, especially when it is combined with conformational analysis and molecular dynamics to understand the EAOPs at molecular scale [164], or to disclose the mechanisms during the organics degradation, the formation of by-products or the production of specific oxidants avoiding toxic species. It can also be useful for the design of electrocatalytic materials for selective degradation or the production of value-added products.

A great number of electrocatalytic materials has been tested to remove different organic pollutants in different water matrices. However, the most relevant theoretical studies have been inspired in the intriguing non-active character of the diamond electrode. For example, pioneering studies were carried out to analyze the electronic structure of BDD using DFT [165–170], describing its surface properties, the energies of the interfacial processes related to water adsorption, and the generation of $\bullet\text{OH}$. The adsorption studies by computational calculations aimed at modeling the diamond surface to understand the effects in surface reactivity due to the boron atoms as dopants, film thickness, sp^2 -impurities or roughness. Although significant developments were achieved in these studies, no micrometric-size surface models were used and only one position boron in the crystal lattice was restricted, avoiding to capture the electrocatalytic properties of BDD. Then, only partial conclusions have been drawn; remaining unrevealed its structural properties and interactions responsible for such behavior. On the other hand, few scientific reports have compressively discussed the energies of the interfacial processes related to water and $\bullet\text{OH}$ adsorption [169,170]; allowing to tentatively elucidate the influence of these processes on the generation of $\bullet\text{OH}$ on BDD. Models under vacuum conditions provided insights about of boron-adsorbate interactions, which were crucial to describe the catalytic activity of BDD. Also, H-terminated diamond surfaces were used for all calculations in few works because these appropriately represent the experimental structures of recently prepared materials [171,172] and these surfaces are more reproducible for heterogeneous reactions involving charge transfer, compared to oxygenated terminations [173,174]. The structure with boron located in tetrahedral coordination, C- sp^3 hybridization and H-saturated BDD surfaces has been considered in theoretical investigations since it has been experimentally demonstrated that these parameters induce a higher electrocatalysis for organic mineralization. A DFT study with O-terminated diamond structures was performed to analyze the $\bullet\text{OH}$ radical formation in alkaline media [169]; whereas water interfaces of BDD saturated by H, O, and $\bullet\text{OH}$ have been theoretically evaluated using DFT-based molecular dynamics to analyze their electrochemical performance [170]. Ab initio modelling was successfully used by Jaimes [175] in order to extend surface models to describe BDD properties by understanding the adsorptions behaviors of H_2O and $\bullet\text{OH}$ radicals in different initial positions, including Van der Waals interactions, confirming the reactivity towards indirect electrooxidation of organic compounds. More recently, the mechanism for water oxidation (with the following main considerations: outer-sphere reaction mechanism, production of $\bullet\text{OH}$ as intermediate, and presence of N, P, S and F elements as dopants on the diamond surface) was studied by means of DFT calculations [162]. Relevant physicochemical considerations, related to the free energy of adsorbed oxygen intermediates (OH^* , O^* and HOO^*) and the maximum ΔG for each one of the oxidation steps, were taken. Based on the findings obtained, ΔG improvements of step H_2O oxidation reactions were calculated, increasing oxygen evolution reaction potential, by using F, S and P as dopants in diamond film, thus, the Faradic

efficiency to produce $\bullet\text{OH}$ was increased. Meanwhile, N dopant favored the oxygen evolution reaction, avoiding its use on EAOPs.

In the case of oxidants, persulfate electrosynthesis was also investigated by computational calculations [176]. As stated in subsection 2.1, the occurrence of $\text{S}_2\text{O}_8^{2-}$ is favored by the formation of $\text{SO}_4^{\cdot-}$ (as principal intermediate), and Davis and co-workers [176] demonstrated experimental and theoretically (by DFT) that formation of $\text{S}_2\text{O}_8^{2-}$ proceeds on higher graphite (sp^2 impurities as active sites) content BDD surface via a two-step mechanism, but it also considered a possible participation of $\bullet\text{OH}$ to form $\text{SO}_4^{\cdot-}$.

Based on the existing literature [162–164,177–179], more electrochemical and theoretical investigations are being developed in order to explain the experimental behavior with molecular structures and electronic properties of pollutants and anodic surfaces, calculating the optimized-geometric structures and the frontier orbitals. These calculations allow evaluating the possible atomic sites (in which the most energetic electrons are localized in frontier orbitals) that can interact between anodic surface and pollutants in direct oxidation mechanisms. On the one hand, potential energy surfaces (PES) can be obtained by using DFT calculations for the oxidation mechanism in order to understand the energy barriers that should be attained for converting pollutant to transition states, before its complete oxidation (Fig. 8b). On the other hand, DFT and the quantum theory of atoms in molecules (QTAIM) can be used as computational tools to understand at a molecular level the electrochemical or chemical reactions taking place by determining the critical points (Fig. 8c) where the electron density distribution is preferentially accumulated in a given plane of the chemical bond (symmetrical and cylindrical distribution).

For example, the EO of carboxylic acids (formic, acetic and oxalic acids) on BDD surface was evaluated by associating experimental results with computational simulations, demonstrating from HOMO energies of acetic and oxalic acids that these compounds are oxidized by a direct electron transfer at the BDD surface coupled with $\bullet\text{OH}$ radicals [162]. Conversely, $\bullet\text{OH}$ generated by water discharge are the responsible of the formic acid oxidation. A novel freestanding and highly-stable 3D SnO_2 -Sb anode with macropores was used to ciprofloxacin (20 mg L^{-1}) oxidation and compared with the effectiveness of BDD electrode [180]. The intermediates were analytically identified, but the ciprofloxacin degradation mechanism on the 3D anode was also elucidated by DFT calculations, demonstrating its concordance of the oxidation pathways followed.

It is evident that the theoretical/computational calculations allow understanding the aspects that impact the oxidation mechanisms/pathways involved during the EO approach or the electronic features at the anode surface, close to it or from the species in solution, as well as from the pollutant structure. Nevertheless, from a computational and experimental point of view, the use of this important tool involves some advantages and disadvantages.

Some considerations to be taken into account are:

- i) reasonable approximations can be achieved,
- ii) a reduction of the number of experiments and the risks is feasible,
- iii) practical accuracy in the approximations associated to experimental expectations,
- iv) better understanding of the reactions on molecular scale to control the design and the development of novel and effective anodes to operate the EAOPs,

Meanwhile, some related issues might be addressed in future, such as:

- i) enough experience on computational methods for their selection,
- ii) limitations to describe intermolecular interactions,
- iii) experience/knowledge to choose the most appropriate theory level for a specific calculation objective, such as functional/basis set/solvation model,

- iv) comparisons/checks with other calculation methods as well as the existing literature, minimizing inaccurate conclusions or misunderstandings,
- v) more interactions between different chemists and physics to collaborate with experienced-users which use sophisticated computational tools and concepts, and
- vi) at the same time, but equally important, more sophisticated studies should be performed in EAOPs to elucidate how the electronic structure of the electrocatalytic materials impacts the conformational dynamic interactions between organic pollutants and electrode surfaces, as well as the multi-point interactions. Nevertheless, water matrices and solvation effects, as well as the oxidants reactions (surface-layer or in the bulk), must be considered in the future.

Finally, it is important to remark that the relationship between experimental and theoretical investigations has allowed confirming the initial EO mechanisms (subsection 2.1) and establishing novel oxidation pathways based on various specific factors.

2.2.4. Using EO for both treatment of organics and disinfection

Regarding the use of electrocatalytic materials in EO-based technologies, the most important insights and progress have been reached on water disinfection, food control and photoelectrochemical methods [96]. The research has been significantly intensified in the last years; however, in the case of water disinfection and food control [26], although several microorganisms have been inactivated or lysed by direct or indirect EO approaches by using different electrodes, important advances on their mechanisms have been mainly accomplished by using BDD anodes.

The destruction of cell walls during EO disinfection is considered as a key factor to justify the cell inactivation. Therefore, the changes of different parameters, such as total protein, K^+ leakage, membrane potential, permeability and protein, lipid peroxidation, intracellular enzyme, cellular ATP level, and DNA fragmentation, has been measured [26], concluding the following:

- i) the damage of the cell walls is induced by the oxidation, via free heterogeneous $\bullet OH$ and persulfate electrogenerated at BDD, of proteins related to the K^+ transport system, in sulfate medium, which hinders both, the subcellular localization of cell division protein and the synthesis of ATP. Additionally, a considerable lipid peroxidation is also attained.
- ii) a total destruction is attained as a whole cell by the intracellular enzymes and membrane proteins were mineralized at BDD, in phosphate medium, and
- iii) the degradation of intracellular enzymatic systems is reached in chloride medium via the action of free heterogeneous $\bullet OH$ and active chlorine species by Cl^- -EO with BDD anode.

Nevertheless, this information was obtained from the findings obtained by the inactivation mechanisms of *Escherichia coli* at different supporting electrolytes or water matrices containing SO_4^{2-} , PO_4^{3-} or Cl^- ions. The use of EO with BDD as water disinfection and organics treatment alternative has been also investigated to inactivate other microorganisms (see Table S2), such as *Pseudomonas aeruginosa*, *total coliforms*, *enterococci*, *Bacilli*, *Clostridium perfringens*, *legionella*, *Microcystis aeruginosa*, *staphylococci*, among others [26]. These should also be studied from a subcellular point of view, as a function of the electrolytic conditions as well as the type and the quality of electrogenerated oxidants, in order to establish their cells inactivation mechanisms as well.

Preventing any kind of food contamination in fresh fruits and vegetables by microbial pathogens, the applicability of EO can also guarantee the water quality, which must be maintained for irrigation or washing practices. Then, microbial risks should be reduced by controlling the irrigation water quality, correct management of water, washing water

treatments or disinfection approaches, re-use of water with good quality and the production of water-based sanitizers. For example, López-Gálvez et al. [181] also evaluated the use of electrodisinfection diamond approach with a Diacell® 101 cell as a technology that helps to reduce the high-water consumption of the fresh-cut produce industry because wash water was reused, having positive economic and environmental impacts. Gómez-López et al. [182] NOM and *E. coli* O157:H7 were removed and inactivated, respectively, from washing water in the washing tank by using electrolyzed waters obtained with different amounts of NaCl (1, 0.5, and 0.15 g L⁻¹). Total bacteria inactivation and a significant decrease on COD due to the organic matter depletion were achieved for vegetable wash water when electrolyzing a solution containing 0.5 g L⁻¹ NaCl. However, low levels of chloroform and trihalomethanes were produced, but they remained below the European limits (100 µg L⁻¹).

2.3. Reactors

As stated in the literature, there are several variables (also mentioned in our previous review [1] and in subsection 2.2) that limit the performance of the EO-based technologies at small, intermediate and industrial scales (Fig. 9), such as:

- i) the anode material,
- ii) the current density
- iii) the temperature,
- iv) the fluid-dynamic conditions,
- v) the nature and concentration of the organic pollutant,
- vi) the supporting electrolyte and conductivity,
- vii) the pH values
- viii) the dissolved oxygen

These relevant aspects were pointed out in our previous review [1], but we have recalled them in this subsection, as parameters of the electrolytic cell, that should be always considered for initial investigations. The operation conditions that should be particularly investigated in future investigation are also mentioned.

On several occasions, a critical discussion on each of the operation parameters has been performed [1,13,36,54,56,63,74]. This approach is useful in some cases; but it is not totally accurate because it omits the possible interactions between the different parameters, especially that between the anode and the supporting electrolyte or solution components [26]. The EO-based approach is strongly influenced and adjusted by the selection of the anode and the composition of the water matrix, which can contain only the organic pollutant and the electrolyte or a mixture of pollutants, solvents, inorganic species, and others. This initial condition causes changes in the electrochemical window, inducing the predominance of specific water-based systems or surface-layer reactions at the anode. In addition, it subsequently affects the volume-based oxidation process in the bulk. For example, the water/ion systems [183], where the ions can be Cl^- , Br^- , F^- or SO_4^{2-} , $C_2O_6^{2-}$, Fe^{3+} , among others. In this case, alterations on the oxygen evolution reaction can be observed, being beneficial or not. Fig. 10 illustrates the current-potential profiles for Pt in the presence of NaCl, NaBr and NaF, promoting variations on the oxygen evolution reaction due to the predominance of H_2O/Cl^- , H_2O/Br^- or H_2O/F^- , respectively (similar study has been also performed at BDD [184]); the production of oxidants or gases as well as promoting direct electron transfer at anodic surface, which consumes the electrical energy supplied to the cell and in some cases, decreasing the EO efficiencies (in terms of the organic molecule removal, as will be discussed in Section 3). In this regard, electrochemical measurements are primarily recommended in order to establish the experimental conditions or to analyze theoretically the effects observed (i.e., voltammetric examination, kinetic and thermodynamic analysis). On the other hand, there are other instrumental techniques that enable the sensitive and selective measurement of inorganic/organic species based

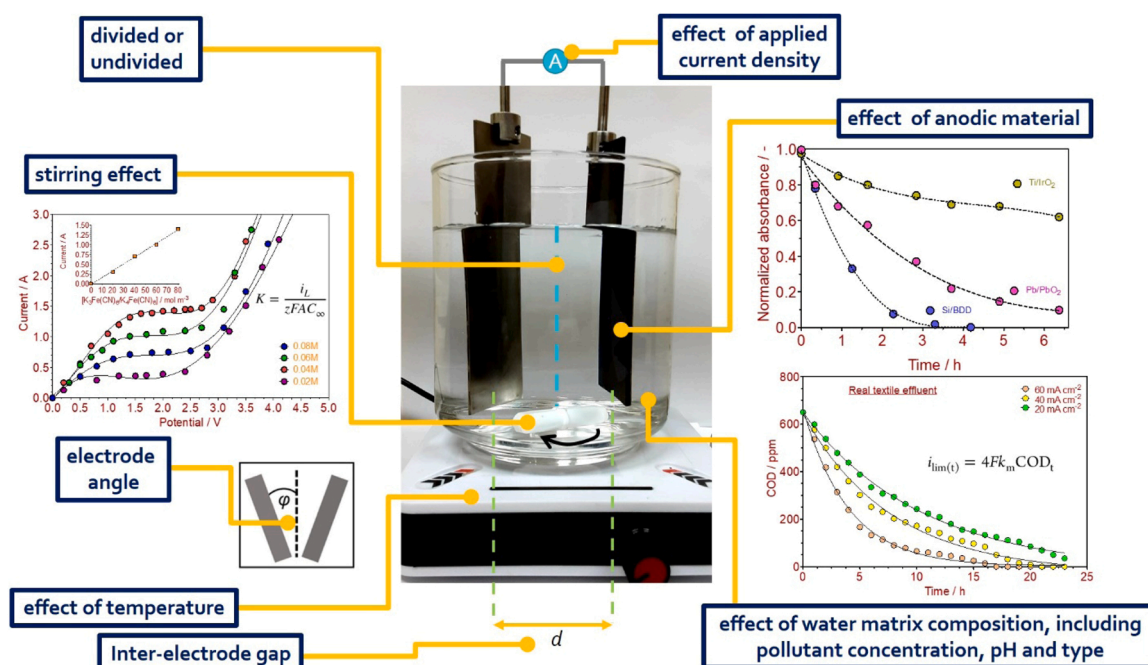


Fig. 9. Overview of crucial but under-explored parameters in some cases, by using a conventional electrolysis cell.

on their specific electrochemical behavior at the working electrode surface. Although some of them have been broadly reported to exhibit superior performance for the determination of surface layers, there are still several major disadvantages. Taking the differential electrochemical mass spectroscopy (DEMS) as an example, this method is limited in describing all produced ionic species precisely, resulting in some unavoidable errors and misjudgments. Second, the comparisons between results in the existing literature and data experimentally obtained by DEMS needs to execute significant considerations for the associations and/or compare with many literature studies. Otherwise, the results could lead to inaccurate or even misleading conclusions because different anodic materials with different features (i.e., preparation, impurities content, dopants and their concentrations, microcrystals or nanocrystals, 2D or 3D surfaces, thickness and roughness, real active area as well as active, non-active or both surface natures) have been compared from literature and experiments. This is the case of diamond films, which have especially demonstrated a versatile behavior or, in other words, an active and non-active nature. For this reason, it is suggested/incentivized that more information about the electrocatalytic properties of the materials tested is reported in the scientific publications, thus avoiding direct comparisons with results already reported for materials that actually are not the same.

In addition to the type of material (i.e. active or non-active anode), the geometry is a crucial factor, which was demonstrated, among others, by Pierpaoli et al. [105] during the EO of sanitary landfill effluents using 3D diamond-carbon nanostructures (Figs. 7a and 7b). The 3D electrodes were significantly more efficient to eliminate the organics from real water matrices when compared with traditional diamond films. Another example is the applicability of DFs, giving extraordinary efficiencies in current and degradation performances to eliminate different organic pollutants from water [117]. These effects are also associated to the mass transport conditions in the electrochemical cell (see above).

When the size or shape, as well as the roughness (using mesh, plate, wire, felt, foam electrodes or surface modifications) are also varied, an increase of the active surfaces and local current density is observed. Also, the cleaning procedure applied to the anode is important because, sometimes, the electrocatalytic material during the EO of synthetic solutions or real water matrices can be susceptible to fouling (adsorption) from promoted side reactions (e.g., polymers or incrustations) [36,63,

134,185,186] or from microorganism [26,134]. For that, no mechanical practice should be adopted; instead, an electrolysis under mild conditions is suggested, as in the case of fragile diamond electrodes [36].

In the last years, the use of divided electrolytic cells has received great attention. On the one hand, when undesired cathodic reactions are to be prevented or also avoiding the migration of ions, gases, byproducts or substrates. On the other hand, when anodic and cathodic processes need to be separated to favor specific conditions or methods, as for example the cathodic production of hydrogen [187] or the cathodic conversion of carbon dioxide [188] the electrosynthesis of high-added value products (at the cathode or anode) [189] or the electrochemical generation of oxidants in a single compartment (at the anode or cathode) [190]. Therefore, the implementation and the type of separator is a crucial choice. The storage of membranes and cleaning procedure are also significant conditions that could influence the EO process.

As already discussed in subsection 2.2.3, self-made electrocatalytic materials and electrolytic cells have been utilized, such as agitated flask, conventional cells with stirring (Fig. 9) or stirred tanks, and flow cells (Fig. 11) in divided or undivided setups [1,13,22,36,63,191]. It can cause variations on the EO efficiencies and reproducibility in diverse laboratories due to the dimensions and the arrangement of the electrodes (angle and distance between the electrodes), the shape-bottom cell (different for beakers or tanks or conventional cells), electric field distribution (homogeneous or heterogeneous, which can favor the formation of deposits or polymerization, as well as surface corrosion), electrode preparation and shape, as well as the stirring conditions in combination with the factors mentioned above promote specific hydrodynamic environments. In fact, even when the cell characterization is not a typical procedure, to determine the mass transport coefficient (Fig. 10c) is also recommended for these EO cells.

Fig. 9 illustrates a conventional EO cell or so called, agitated flask or stirred tank, which is a common option in the laboratories due to its specific advantages, such as [1,22,63,191]:

- dry and safe electrical connections to study the effect of I_{app} or E_{cell} ,
- easy method to collect the sample as a function of predetermined time periods,
- easy addition of the supporting electrolyte or solutions,

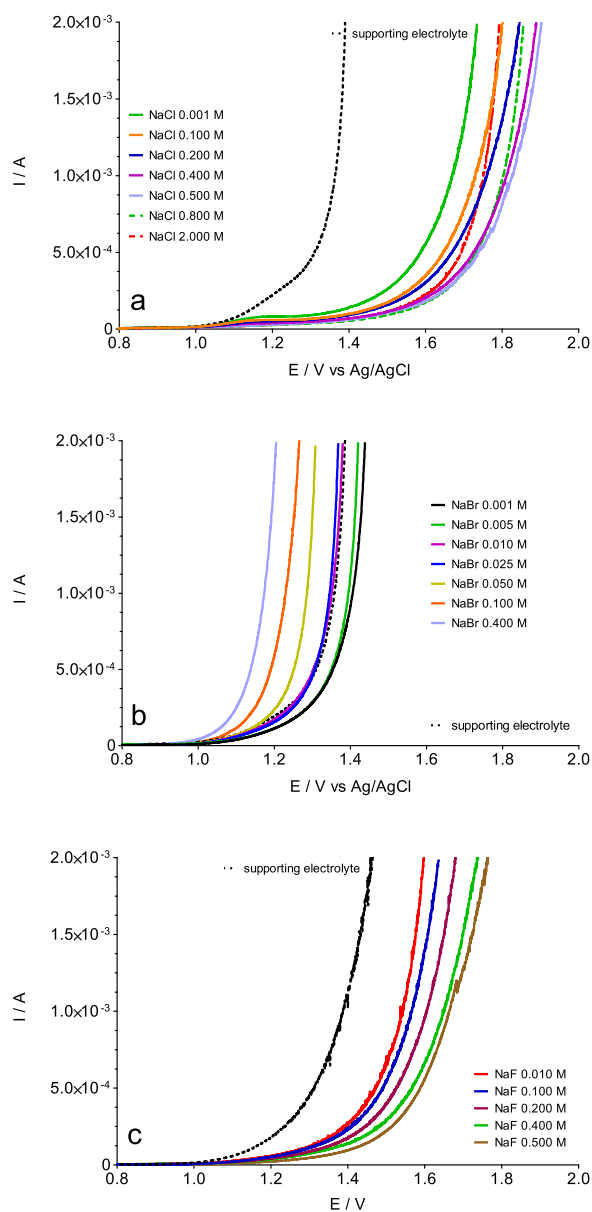


Fig. 10. Current-potential curves for the Pt electrode in the presence of different amounts of (a) NaCl, (b) NaBr and (c) NaF in solution by using 0.25 M NaOH + 0.5 M Na₂SO₄ as supporting electrolyte at scan rate of 5 mV s⁻¹. Adapted with permission from [183]. Copyright Electrochemical Society Inc. 2017.

- iv) simplicity on the electrodes modification (position, distance, arrangement and retrieval) avoiding to drain the cell,
- v) appropriate mixing and stirring solution, allowing the homogenization of the water matrix in order to enhance the mass transport by pollutant diffusion/convection toward the electrodes surface and of the intermediates from them,
- vi) heating using a magnetic stirrer/hot plate for temperature regulation,
- vii) suitable measurements of the electrode potential and their distribution in the cell,
- viii) a possible kinetic analysis of water matrices treatment, and
- ix) easy continuous pH adjustment.

However, the use of an undivided beaker or undivided stirred tank reactor has some disadvantages [191]:

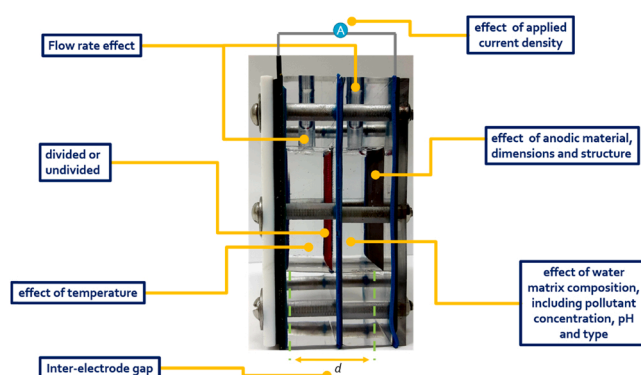


Fig. 11. Overview of crucial parameters when using a flow electrochemical cell.

- i) apparent experimental conditions that are not completely fixed,
- ii) irreproducible and undefined operation parameters and, consequently, the oxidation reaction environment is difficult to be scaled-up,
- iii) water matrices, effluent and solution composition are not completely considered for EO experiments, [22]
- iv) the determination of the limiting current density (i_{lim}) is not considered to establish the control regime (charge or mass transport regime), [1,22]
- v) no hydrodynamics or fluid dynamics characterization to obtain the mass transfer coefficient (k_m), [1]
- vi) considerations regarding the ion strength and conductivity; in the former, the ions to give sufficient conductivity are added, but these ions can participate as oxidant precursors or scavengers; in the latter, similar values of conductivity can be reached by using different ion concentrations, thus affecting the performance. Then, appropriate factor selection is needed.

A strong effect of mechanical stirring on the outcome of a batch-type electrolysis can be observed because the heterogeneous reaction takes place at the anode surface; mass transport by stirring plays a key role transporting the pollutants/intermediates/ions towards the electrode surface, as already above. On the other hand, an effect should be expected by varying the distance between the electrodes; however, it has been slightly examined. Perhaps, the electrode distance impact over the EO of organics is related to the electrical field distribution, which generates hot-current points that modify their effectiveness to mineralize organics or to produce oxidants. In this context, the use of a precise electrode distance would contribute to guarantee electrochemical conversion/combustion in short treatment times and decreasing the ohmic resistance. Extremely small inter-electrode distances are currently recommended [192–194]. Therefore, flow cells with thin-gap or zero-gap [22,186,192–194] exhibit great advantages over batch reactors due to their excellent mass transport conditions, processing in continuous mode and lower ohmic resistance. In addition, it is possible to work with this type of flow cells reducing dramatically the supporting electrolyte concentration or operating without it. For this reason, the use of flow electrochemical cells is the better EO strategy for scaling-up the process.

Finally, the temperature generally has an impact on the ionic conductivity, mass transport, and electrosynthesis of oxidants, and subsequently, it is beneficial for the EO performance. However, the application of high current densities leads to a temperature increase and hence, an external cooling jacket is needed.

As a partial conclusion, it is evident that more investigation should be focused in designing/constructing/optimizing the electrolytic cells without under-estimate none of the possible operation parameters. However, the water matrices composition and real wastewater should be a priority, not only as a “new fashion condition” to be studied with all

possible organic pollutants again (in other words, repeating, once again, the organic contaminants that have been already studied in the past), but as a source of essential information to translate the electrochemical technology from lab to commercial devices. Also, the concentration of organics is a controversial parameter, however, different environmental laws with different pollutants limits are valid in different countries as well as the pollution levels attained in various countries are different, then, it should be considered in combination with other electrochemical-chemical-technological operation factors.

The classical plane parallel electrode geometry has been extensively incorporated to flow reactors due to many practical advantages (Fig. 11). The reaction environment in these cells has been both experimentally and theoretically described, especially in relation to fluid flow, fluid dispersion, mass transport, potential distribution and concentration change. Appropriate selection of electrodes is recommended, mainly encouraging to search and test novel materials in significant dimensions. By using flow reactors, critical operation conditions, including materials that are used as anode and cathode and water matrices composition, should be widely studied to better understand the influence of competitive reactions, synergistic or antagonist effects and production of oxidants in EO-based technologies.

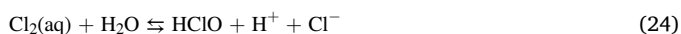
On the other hand, by understanding the use of divided or undivided flow reactors, based on the selection of the applicability (i.e., the importance on both cathodic and anodic reactions), it is possible to control the cell potential due to the implementation or not, of a membrane or separator and, consequently, modulate the production of oxidants, electrical requirements and costs. A more detailed discussion will be made in the last section of this review.

3. Oxidation of organic pollutants by electrogenerated active chlorine

3.1. The process

Based on the existing literature, which has been summarized and discussed in authoritative reviews and books [1,13,16,22,32,44,45], oxidation by electrogenerated active chlorine is considered as one of the most interesting alternatives to chemical chlorination for water and wastewater decontamination and disinfection. It is an in situ treatment which allows electrogenerating active chlorine species to degrade different organic pollutants and/or inactivate various waterborne agents. Indeed, when chloride ions are naturally present or spiked into an aqueous matrix, their oxidation at suitable catalytic anodes gives rise to the formation of a mixture of oxidants that contribute to the degradation and even the mineralization of organic pollutants, both at the anode surface and in the bulk solution. The concentration predominance, the half-life time and the oxidation power of the active chlorine species depend on the pH conditions of solutions and on water matrices composition. As mentioned in Section 2, numerous oxidants, either chlorinated or non-chlorinated, can be produced in situ as detailed hereby [1,32,195]:

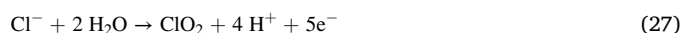
i) **Active chlorine.** The anodic oxidation of chlorides yields dissolved chlorine (reaction (23), $E^\circ = 1.36$ V vs. SHE)), which can evolve towards HClO (reaction (24), $E^\circ = 1.49$ V vs. SHE) and ClO^- (reaction (25), $E^\circ = 0.89$ V vs. SHE), upon successive acid-base equilibria. These three chlorinated compounds, commonly known as active chlorine, can oxidize the organic molecules in the homogeneous phase (i.e., the liquid phase). ClO^- prevails at alkaline pH, HOCl under mild acidic conditions and Cl_2 is the predominant species in very acidic media (pH lower than 2), where the formation of chlorine bubbles can occur.



ii) **Adsorbed chloro and oxychloro radicals.** The treatment of organic molecules by electrogenerated active chlorine usually leads to a higher abatement, as compared to the analogous non-electrochemical process with HClO added in the form of a chemical reagent, owing to the contribution of additional oxidants such as adsorbed hydroxyl radicals, which are formed from the catalytic anodic oxidation of water (see Section 2), as well as highly reactive chloro and oxychloro species generated from chloride oxidation (Fig. 12 and reaction (26)) [196–198].



i) **Cl_2O and ClO_2 .** Chlorides can be also converted into Cl_2O and ClO_2 by chemical or anodic (reactions (27) and (28)) routes, as recently pointed out by Mostafa and co-authors after an analysis by differential electrochemical mass spectrometry for BDD anodes [199]. These routes can depend on the features of adopted electrocatalyst. As an example, at BDD they may depend on many characteristics such as sp^3/sp^2 ratio, roughness, thickness, support and boron doping (see subsection 2.3). These species are considered very interesting, since ClO_2 is a powerful oxidant that does not lead to the formation of potentially toxic chlorinated byproducts [199,200], whereas Cl_2O is one of the most active oxidants [201].



In the last two decades, it has been shown that the abatement of organic pollutants by electrogenerated active chlorine is very effective, since in many cases high removal rates can be obtained, in concomitance with an almost complete mineralization. Moreover, this is feasible with high current efficiencies for many kinds of wastewater and organic pollutants [29,202–206]. Examples of water matrices that can be effectively treated by electrogenerated active chlorine include industrial wastewater contaminated by refractory organic compounds [207] or pharmaceutical residues [208], reverse osmosis concentrates [209], landfill leachates [210], as well as olive oil mill, dairy and textile wastewater [211,212] and tannery [57] and petrochemical effluents [213–215]. Furthermore, as shown in various studies, higher and faster removals of organic pollutants are achieved as compared to those obtained using chlorinated chemical oxidants [204,205]. However, this

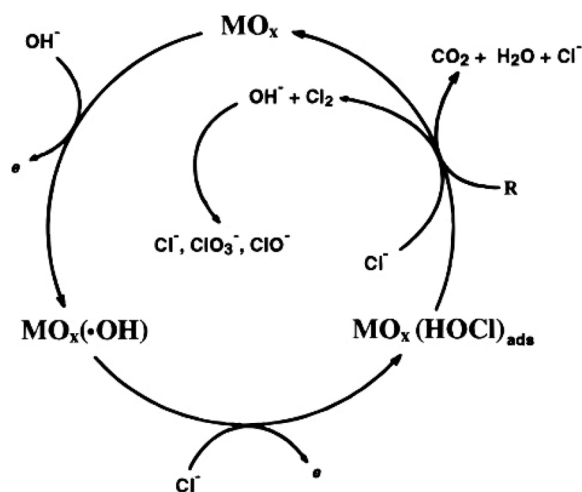


Fig. 12. Reaction pathway proposed by De Battisti and co-authors for the electrochemical incineration mediated by active chlorine. Adapted with permission from [6]. Copyright Electrochemical Society Inc. 2000.

method presents various and remarkable disadvantages discussed in detail in the following subsection. In the last few years, various authors have tried to solve these problems using different and innovative strategies that are summarized below.

3.2. Main problems and suggested solutions

As partially discussed in the previous review of the authors [1], a wider application of electrogenerated active chlorine to the treatment of wastewater contaminated by organic pollutants was somewhat limited in the last years due to some important potential problems:

- in order to enhance the removal of organic compounds and the current efficiency, as well as to select the most suitable operation conditions, it is necessary to carry out quite complex and focused optimization studies;
- the formation of toxic organochlorinated derivatives was reported in many studies;
- the formation of oxychlorine anions such as ClO_3^- and ClO_4^- , which potentially present negative effects on human health, can occur.

In the following paragraphs, the main relevant and recent findings related to these problems are reported and critically discussed.

3.2.1. Enhancement of organics removal and current efficiency

A large number of studies was devoted in the last two decades to the optimization of the operation conditions with the main aim of enhancing the removal of organics and the current efficiency. It was shown that there are no general rules valid for all the cases since the optimization of the process strongly depends on the nature of the pollutants and on the composition of the wastewater. However, the literature provides very useful insights that can strongly help the optimization study when a new case must be solved. In our previous review published in 2015, the effect of the operation conditions (nature of the anode, pH, current density, hydrodynamic conditions, etc.) on the removal of organic pollutants (and on current efficiency) mediated by electrogenerated active chlorine was discussed in detail [1]. However, in the last few years, it was highlighted that the experimental conditions should be carefully selected not only in order to maximize the removal of organic pollutants, but also to minimize the formation of potentially toxic chlorinated byproducts. In particular, several important and recent contributions allowed to better clarify the effect of operative parameters on the removal of organic pollutants and of TOC and on the minimization of the concentration of several by-products, as described more in depth in the following paragraphs. In general, when significant amounts of chlorides are present (or purposely added) in the aqueous matrix and the organic pollutants are easily oxidized by electrogenerated active chlorine, MO catalytic anodes such as RuO_2 and IrO_2 are preferable due to their high current efficiency for the active chlorine generation (Fig. 13) and their relatively low cost [1].

IrO_2 -based electrocatalysts seem a very interesting option because they also yield a low concentration of chlorinated byproducts (see subsections 3.2.2 and 3.2.3) when compared to many other electrodes. Conversely, at low concentrations of chlorides and/or for the treatment of organic pollutants particularly resistant to electrogenerated active chlorine, non-active anodes such as BDD could be chosen. Indeed, these electrocatalysts were reported to generate high amounts of active chlorine coupled with the formation of very reactive hydroxyl radicals under suitable operative conditions [217]. Anyway, in this case, focused studies have to be carried out in order to avoid the formation of toxic chlorinated products, as detailed below. As an alternative, in such cases, the utilization of TiO_2 nanotube-based anodes could be considered, even if further studies are necessary to optimize the process with these promising electrocatalysts (see Section 2) [217].

Using metal oxide catalysts as the anode, which has been the most usual choice so far, higher abatements of organics and current

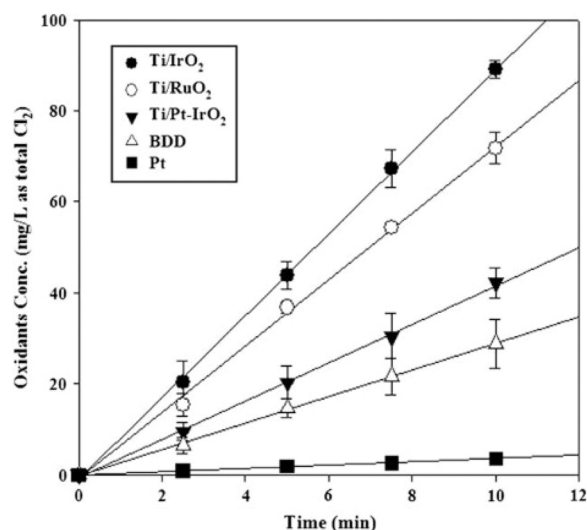


Fig. 13. Effect of the catalytic anode material on the evolution of active chlorine ($i = 17 \text{ mA cm}^{-2}$, 0.017 M NaCl , 25°C).

Adapted with permission from [216]. Copyright Elsevier B.V. 2009.

efficiencies are obtained for most systems presenting high chloride concentrations, at low mixing rate (or flow rate) and at neutral or low pH, although some exceptions exist [1]. A complex effect of current density is reported; indeed, the use of high current densities leads to a larger formation of active chlorine and of other oxidants (see Fig. 14 for the formation of chlorine and ClO_2^- during the electrooxidation of actual wastewater with a BDD anode), as well as to a faster mineralization of organics [1]. However, a low current density coupled with a long electrolysis is preferred in order to avoid or minimize the formation of chlorate, perchlorate and organochlorinated compounds (see subsections 3.2.2 and 3.2.3).

Recently, trials performed with BDD, $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$ and Ti/RuO_2 anodes showed that the abatement of organics can be strongly enhanced using suitable cathodes like carbon felt and silver. In addition, a system with one anode and two cathodes (carbon felt and silver) allowed enhancing the removal of organic intermediates and minimizing the formation of chlorinated by-products such as chloroacetic acids, chlorate and perchlorate [218], as detailed in the following paragraphs. In particular, the utilization of both two cathodes and low current densities yielded very interesting results.

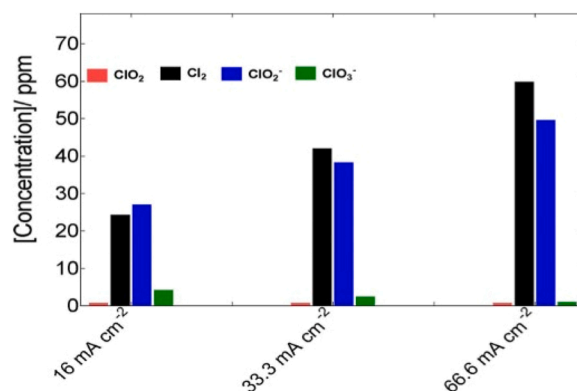
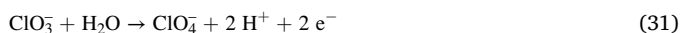
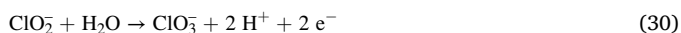
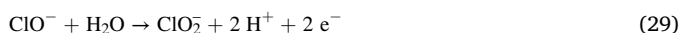


Fig. 14. Electrogenerated reactive chlorine species (RCS) found in the treated real washing machine effluent after 360 min of electrooxidation treatment with BDD.

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3.2.2. Formation of chlorate and perchlorate

The formation of chlorate (reactions (29) and (30)) and perchlorate (reaction (31)) during the electrolysis of aqueous solutions containing chlorides was widely studied in the last years [29,32]. It was proposed that these compounds can be formed by various routes (reactions (29)–(34)) and that their generation can be favored by the occurrence of relative high amounts of reactive hydroxyl radicals.



Very high concentrations of chlorate and/or perchlorate were detected using different anodes for the electrochemical treatment of various liquid effluents such as reverse osmosis retentates [209], latrine wastewater [219] and urine [220]. Based on the literature, it seems that various parameters affect the generation of these compounds, including mainly the nature of the catalyst selected as anode. In particular, since the work of Bergmann in 2009, it was shown that the electrolysis with BDD yields a concentration of perchlorate about two orders of magnitude higher as compared to that obtained observed with Pt, RuO₂- and IrO₂-based anodes [221]. BDD also yielded a high initial concentration of chlorate that was, however, almost completely converted to perchlorate after a sufficiently long period [222]. The high generation of chlorate and perchlorate at BDD was, in particular, attributed to the peculiar ability of such electrocatalyst to generate significant amounts of very reactive hydroxyl radicals under anodic polarization (see Section 2), thus accelerating the oxidation of chlorides to these products. As described in Section 2.2.2, boron doping level and sp²-impurities on BDD surface strongly modify their adsorption properties, affecting its oxidation power and/or its capacity to produce specific oxidizing species. In particular, it has been recently reported that the production of chlorates and perchlorates from chloride-water matrices can be minimized, using a higher sp³ content [111].

In this context, Bagastyo et al. [209] have shown, for the anodic oxidation of reverse osmosis concentrate using various MO anodes, that chlorate was the only inorganic chlorinated species formed, with the highest concentrations attained using Ti/SnO₂-Sb, followed by Ti/Pt-IrO₂ and Ti/PbO₂, whereas the lowest values were detected using

Ti/IrO₂-Ta₂O₅ and Ti/RuO₂-IrO₂ (Fig. 15). Similarly, Hao et al. [218] found, during the treatment of phenol solutions, maximum concentrations of chlorate using BDD, followed by Tu/RuO₂ and Ti/IrO₂-Ta₂O₅. In these three cases, perchlorate was found only with BDD.

TiO₂ nanotube-based anodes, furthermore, give rise to significantly lower concentrations of chlorate and perchlorate, as compared to BDD; indeed, as reported by Yang and Hoffmann for the electrolysis of human wastewater at 5 mA cm⁻², under the operation conditions that yielded 18 mM chlorate and 3 mM perchlorate using BDD, only 6 mM chlorate and no perchlorate were found using TiO₂ nanotube-based anodes [217]. These results may in part be attributed to the fact that these electrocatalysts were reported to generate more active chlorine and less •OH than BDD [217]. A second important parameter that strongly affects the formation of perchlorate is the current density. Indeed, a larger formation of chlorate and/or perchlorate, upon the increase of the current density, has been reported with both BDD [217,218,221–223] and IrO₂-based anodes [218,224]. As an example, the electrochemical treatment of a secondary effluent from a municipal sewage treatment plant, containing 29 target pharmaceuticals and pesticides and 8.6 mM Cl⁻ ions, yielded a concentration of perchlorate close to 1 mM and lower than 0.25 mM at 19.6 and 9.8 mA cm⁻², respectively, using a BDD anode at pH 7 [222]. Furthermore, Cano and co-authors [223] reported, for the electrolysis of effluents of municipal wastewater treatment facilities with BDD, that it was possible to almost avoid the formation of chlorate and perchlorate by working at very low current densities of 0.13 mA cm⁻²; however, this value was too low to achieve a fast removal of organic pollutants. Jasper et al. [224] reported no formation of perchlorate using TiO₂/IrO₂ for the electrochemical treatment of latrine wastewater; furthermore, the concentration of chlorate decreased when working at lower current densities, and it was lower than that achieved using BDD; however, at all adopted operation conditions (2.5–7.5 A L⁻¹, 30 mM Cl⁻), the concentration of chlorate was above the World Health Organization (WHO) drinking water guidelines [224]. Overall, it seems that chlorate and perchlorate generation may be potentially avoided or minimized coupling the utilization of not-active anodes and low current densities [225]. In particular, Schaefer and co-authors have shown, for the electrochemical treatment of surface water with a Ti/IrO₂ anode, that the concentration of chlorate and perchlorate can be limited under the regulated levels by working at low current densities (0.25–8 mA cm⁻²) [226]. However, further research is necessary in order to better assess the possibility of using IrO₂-based electrocatalysts as anodes in order to effectively remove organic contaminants in the presence of chlorides, limiting the formation of chlorate below the regulated levels.

Since BDD leads, on the one hand, to very fast and high abatements of organics, and, on the other hand, to high concentrations of chlorate and perchlorate, numerous studies were devoted in the last few years to look for operation conditions that allow minimizing the formation of ClO₃⁻ and ClO₄⁻ during the electrolysis of aqueous solutions with this anode. In particular, the perchlorate production using BDD was decreased using a low current density (see above), a high flow rate [221], a higher sp³ content [111] and a significant concentration of organics [227,228] that causes the depletion of hydroxyl radicals. The group of Serrano [228] has shown, for the treatment of wastewater containing pharmaceuticals using BDD, that the application of a current density close to *i*_{lim} favors the conversion of chloride to hypochlorite; conversely, at current densities above *i*_{lim}, ClO⁻ was further converted mainly to ClO₄⁻.

It is worth to mention that perchlorate can be reduced using various electrocatalysts like Fe, Pd-Fe, Pd or Cu as cathodes [225]. As an example, using a Rh-Cu/stainless steel cathode, a reduction of 78% of initial perchlorate to chloride (95% selectivity) was reported [229]. Similarly, Wang et al. [230] have shown that perchlorate reduction took place in the concentration range of 2–100 ppm at room temperature, giving rise to chloride as the major end product at numerous cathodes including Sn. Hence, it would be interesting to evaluate the potential use

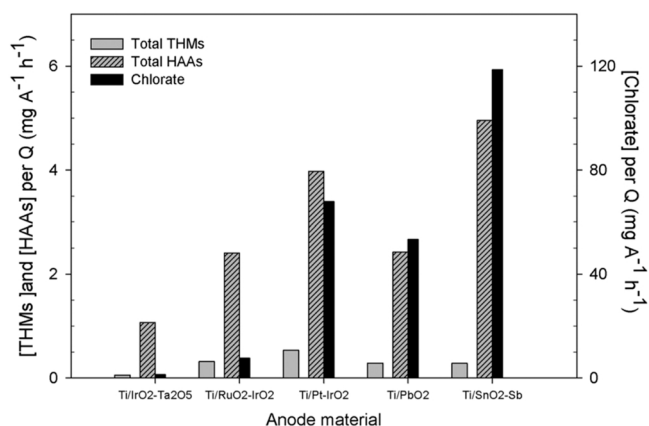
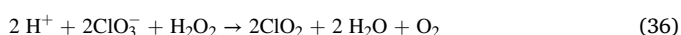
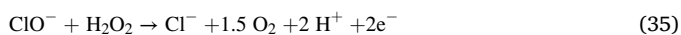


Fig. 15. Concentrations of total trihalomethanes (THMs), haloacetic acids (HAAs) and chlorate observed using various anodes for the electrochemical treatment of reverse osmosis concentrate, after supplying a specific electric charge of 0.55 Ah L⁻¹.

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of such kind of cathodes in undivided cells in the context of the treatment of organics in wastewater containing chlorides. However, as reported by Yang in 2020 [217], usually long electrolyses are required for the electrochemical ClO_4^- reduction. Another option may consist of the utilization of undivided cells equipped with carbonaceous cathodes, such as carbon felt; indeed, these cathodes convert oxygen to H_2O_2 (see Section 4), which can limit the formation of chlorate and perchlorate, as recently shown by the group of Rodrigo during the electrochemical reclamation of urban treated wastewater [231]. H_2O_2 reacts with hypochlorite [232,233], causing its reduction to chloride (reaction (35)), and with chlorate to yield ClO_2 (reaction (36)). In particular, chlorine dioxide is currently considered an excellent oxidant, even when its production can be considered as a parasitic reaction. It has been electro-synthesized, using undivided electrochemical or divided cells by anodic oxidation of hypochlorite or cathodic reduction of chlorate, to be used as disinfectant or strong oxidant in water treatment, achieving interesting results [34].



As mentioned above, the utilization of carbon felt cathodes was recently investigated using either MO or BDD anodes for the electrochemical remediation of phenol in water containing chlorides. It was found that the utilization of carbon felt allowed both enhancing the TOC removal and reducing the concentrations of chlorate and perchlorate [218].

Another important parameter that affects the generation of chlorate and perchlorate at BDD is the concentration of NaCl. Indeed, in the case of the electrochemical treatment of water solutions of phenol in undivided cell equipped with BDD anode and Ni cathode, the increase of NaCl concentration from 0.5 to 5 M resulted in a significant decrease of the final concentration of chlorate. This result is probably due to the fact that the generation of chlorate is favored by the presence of hydroxyl radicals, whose formation is hampered at high NaCl concentrations. Moreover, no formation of perchlorate was detected when the electrolysis was performed at 5 M. However, the increase of NaCl concentration resulted also in a decrease of TOC removal. In particular, at low concentration of chlorides, where the hydroxyl radicals generation is expected to be more important, a higher removal of TOC was achieved using BDD (74%) which produces very reactive hydroxyl radicals, with respect to that obtained at Ti/RuO₂ anodes (43%). Conversely, at high concentrations of NaCl, where the active chlorine generation is expected to prevail, a higher abatement of TOC was achieved using Ti/RuO₂

instead of BDD (50% vs. 39%), thanks to the greater effectiveness of the former anode to produce active chlorine [218].

3.2.3. Formation of organochlorinated derivatives

The potential generation of organochlorinated derivatives, such as chloroaromatic and chloroaliphatic compounds and, in particular, of chloroacetic acids (HAAs) and chloroform, due to substitution and addition reactions between organic pollutants and active chlorine, is among the most important drawbacks in IEO. Indeed, chloro-organic substances can be in many cases more toxic and resistant to the mineralization than their parent compounds. As an example, Deborde and von Gunten have shown that, due to the activation of the ortho/para directing hydroxyl group, the chlorination of phenol proceeds via a stepwise substitution of the 2, 4 and 6 positions, and that the phenoxide ion reacts 105 times faster than the neutral form of phenol (Fig. 16) [234].

In this context, Comninellis and Nerini showed that the chemical oxidation of phenol with NaClO (10 mM) gives rise to the formation of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol [235].

According to various studies, chlorophenols are formed in the first stages of the anodic oxidation of phenol using different anodes, but they can be removed in the last stages upon sufficiently long electrolysis. For example, the electrochemical mineralization of phenol (912 mg L⁻¹) in aqueous solutions with NaCl (120 g L⁻¹) using carbon electrocatalysts at a current density of 32.9 mA cm⁻² led to the formation of *p*-chlorophenol, *o*-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol, which presented a maximum concentration after about 1–4 h [236]. However, all these byproducts were removed after 10 h [236]. Similar results were found during the electrolysis of solutions of phenol in NaCl medium (0.50, 0.22 and 0.36 M) with Ti/PbO₂ anodes, at alkaline pH and 100 mA cm⁻²; after supplying 4 Ah L⁻¹, the presence of chlorophenols was observed at all chloride concentrations, but after 8 Ah L⁻¹ the cleavage of the aromatic ring took place and mainly carboxylic acids and alcohols were accumulated [237]. However, under all adopted operation conditions, the formation of chloroform occurred [237]. Similarly, only CHCl₃ was formed during the electrolysis of aqueous solutions of phenol with 1.05 M Na₂SO₄ and 85 mM NaCl using Ti/SnO₂ and Ti/IrO₂ anodes [235]. More recently, Zambrano and Min have reported that the anodic oxidation of phenol with a Pt/Ti electrode at 9.6 mA cm⁻² in the presence of NaCl (10 g L⁻¹) gave rise to the formation of chloroform and 1,2-dichloroethane that were, however, degraded by the end of the electrolysis [238]. Similarly, Hao et al. [218] have found that using various anodes (BDD, Ti/RuO₂ and Ti/IrO₂-Ta₂O₅) the

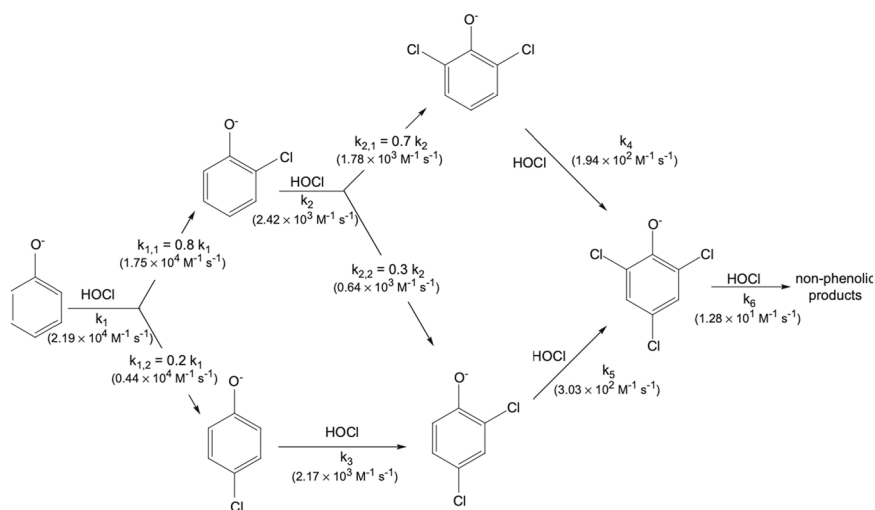


Fig. 16. Reaction scheme for the chlorination of phenoxide ion with rate constants and ratios percentage obtained. Adapted with permission from [234]. Copyright Elsevier B.V. 2007.

degradation of phenol in water containing chlorides yielded chlorophenols that were removed in a short time with the formation of carboxylic and chloroacetic acids.

Similarly, during the treatment of wastewater contaminated by some pharmaceutical compounds (sulfamethoxazole, propranolol and carbamazepine), the formation of seven halogenated intermediates (3,5-dichloroaniline, 2,4,6-trichloroaniline, 9-chloroacridine, 2-chloro-1,4-benzoquinone, 2-chlorocyclohexanone, dichloroacetic acid and chloral hydrate) was observed after 4 min when the electrolysis was performed in the presence of NaCl using a BDD anode; after 90 min, a significant decrease of the byproducts was observed [208]. In the last years, it has been pointed out that the electrochemical treatment of wastewater contaminated by organics in the presence of chlorides can give rise to the formation of HAAs, which are rather resistant compounds. As an example, in the case of the electrochemical treatment of latrine wastewater, chloroform, monochloroacetic, dichloroacetic and trichloroacetic acids were detected using either MMO or BDD anodes [224]. HAAs were initially formed at faster rates on BDD anodes as compared to $\text{TiO}_2/\text{IrO}_2$ anodes; however, with BDD the chlorinated HAAs reached a peak concentration after 1–2 h, whereupon they gradually disappeared, whereas using $\text{TiO}_2/\text{IrO}_2$ they continued to accumulate over time [224]. A detailed analysis of the effect of the nature of the anode on the formation of chlorate and perchlorate (see the previous subsection), as well as of THMs like chloroform and HAAs was performed by Bagastyo and co-authors [209] during the electrochemical treatment of reverse osmosis concentrate from an advanced water treatment plant located in Australia. Five anode materials with different oxidation power, i.e., active ($\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$, $\text{Ti}/\text{RuO}_2\text{-IrO}_2$, and $\text{Ti}/\text{Pt-IrO}_2$) and non-active (Ti/PbO_2 , and $\text{Ti}/\text{SnO}_2\text{-Sb}$), were selected. It was shown that the nature of the anode strongly affects the formation of both THMs and HAAs (Fig. 15). Indeed, the total concentration of HAAs decreased in the order $\text{Ti}/\text{SnO}_2\text{-Sb} > \text{Ti}/\text{Pt-IrO}_2 > \text{Ti}/\text{RuO}_2\text{-IrO}_2 > \text{Ti}/\text{PbO}_2 > \text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$. Similarly, the amount of THMs formed during electrochemical oxidation decreased in the order $\text{Ti}/\text{Pt-IrO}_2 > \text{Ti}/\text{RuO}_2\text{-IrO}_2 > \text{Ti}/\text{SnO}_2\text{-Sb} > \text{Ti}/\text{PbO}_2 > \text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ [209]. The good results obtained using the IrO_2 -based anodes were confirmed by Schaefer and co-authors, who have shown, in the case of the disinfection of surface water, that at low current densities (0.25 or 1 mA cm^{-2}) an effective disinfection can be obtained with this anode, limiting the concentrations of THMs and HAAs below regulated limits [226].

Despite these promising and interesting results, it seems that further studies are necessary to better clarify the possibility to completely avoid or minimize the accumulation of organochlorinated byproducts at the end of the electrolysis. In particular, it would be very useful to better evaluate the effect of various catalytic cathodic materials on the performance of the process, focusing on catalysts that can reduce organochlorinated compounds. As mentioned more in detail in subsection 4.1, Ag, Fe, Pd, Cu, and graphene-based cathodes were reported to exhibit good performance for the reduction of various halogenated compounds. As an example, it was shown that chloroethanes [239,240] or chloroacetic acids [241] can be partially de-halogenated at silver cathodes. The abatement of 1,1,2,2-tetrachloroethane was also performed in undivided cells using a BDD anode and a silver cathode, both in a conventional and in microfluidic cell; it is worth to mention that in the microcell an almost total removal of this very resistant chlorinated compound was achieved [242]. In this context, Hao et al. have recently shown, for the electrochemical treatment of water solution of phenol, that the concentration of HAAs formed upon use of BDD or metal oxide anodes can be strongly reduced by employing a silver electrocatalyst as cathode, which is able to convert these halogenated compounds to corresponding acetic acids that can be more effectively oxidized by active chlorine [218]. Indeed, the use of silver cathode allowed to enhance also the TOC removal. As mentioned in the previous paragraph, an interesting alternative consists of the utilization of carbon felt cathodes in order to reduce oxygen to H_2O_2 that can react with hypochlorite to give chlorides (reaction (35)), and with chlorate to give ClO_2

(reaction (36)), reducing the amounts of chlorinated byproducts including chlorate, perchlorate and chloroacetic acids [231,243]. Another route may consist in the adsorption of chlorinated compounds by granular activated carbon and on its conversion to a cathode to degrade them by electrolysis [244].

Eventually, the utilization of an undivided cell equipped simultaneously with two cathodes (carbon felt and Ag), was proposed [218]. As shown in Fig. 17A, the substitution of a Ni cathode with two cathodes gave rise to a strong increase in the removal of TOC using a $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode (the removal of TOC increased from 44% to 67%). Similarly, using a BDD anode, the removal of TOC was close to 74% and 86% using Ni and Ag-CF cathodes, respectively. It is worth to mention that the system with two cathodes gave a significant improvement of the removal of TOC (Fig. 17 A) and of CE_{TOC} (Fig. 17B) mainly in the last part of the experiments, because Ag and carbon felt cathodes were able to convert organics that were formed during the electrolyses, such as HAAs (Fig. 17B). Moreover, a relevant decrease of the concentration of chlorate and perchlorate was obtained using Ag and carbon felt cathodes with respect to the experiments carried out with Ni cathode.

3.3. Coupling strategies

3.3.1. Coupling with electrochemical disinfection

Many authors have shown that electrogenerated active chlorine can be used effectively, using suitable anodes and operation conditions, to inactivate a large variety of microorganisms ranging from bacteria to viruses and algae [25,32,216,225,226]. Hence, the treatment with electrogenerated active chlorine can be potentially used for the simultaneous mineralization of organic pollutants (i.e., water decontamination) and water disinfection. Furthermore, also the production of sterile water for medical, biological, and food safety applications can be performed [25,26]. The most adopted method for drinking water disinfection consists of the addition of chlorine and/or chlorine byproducts that can eliminate the most dangerous microorganisms. However, this method presents some disadvantages like bad odor and taste, low removals for some resistant microorganisms, the potential formation of toxic products such as THMs and the dangerous transportation, storage and manipulation of chlorine gas. Electrocatalytic-chlorination presents some potential advantages such as the in situ generation of disinfectants, thus limiting the risks associated to storage and handling, and a higher disinfection efficiency [25,245,246]. Indeed, various authors have found more rapid inactivation as compared to chemical chlorination for several microorganisms like *Escherichia coli*, the rugose strain of *Vibrio cholerae*, the bacteriophage MS2, *Clostridium perfringens*, and *Bacillus subtilis* spores, owing to the involvement in the electrochemical route of a mixture of oxidants (see subsection 3.1) [247,248]. Furthermore, some authors have reported that disinfection via electrochemical treatment can result in lower generation of THMs than conventional chlorination [249]. Many kinds of anodes can be used, including MMO, which favor the generation of active chlorine, and BDD that generates larger amounts of hydroxyl radicals. The latter yields a very fast inactivation, but also a higher production of toxic chlorinated byproducts (see 3.2.2 and 3.2.3). DSA such as IrO_2 -based electrodes coupled with low current densities are preferred, in order to avoid surpassing the limits for THMs, HAAs and perchlorate concentrations. However, the utilization of BDD seems viable to achieve fast removals of microorganism if the generation of toxic byproducts is avoided by working under selected operation conditions, especially low current densities [223], and the advances on the electrochemical BDD disinfection systems should allow the technological translation of the concepts from home-made cells to commercial BDD-disinfection devices, as will be discussed in Section 5.

3.3.2. Coupling with reverse electrodialysis

Recently, it has been proposed to drive electrochemical treatment of wastewater by renewable sources and, in particular, by salinity gradients. Salinity gradients widely available in nature (estuaries or mixtures

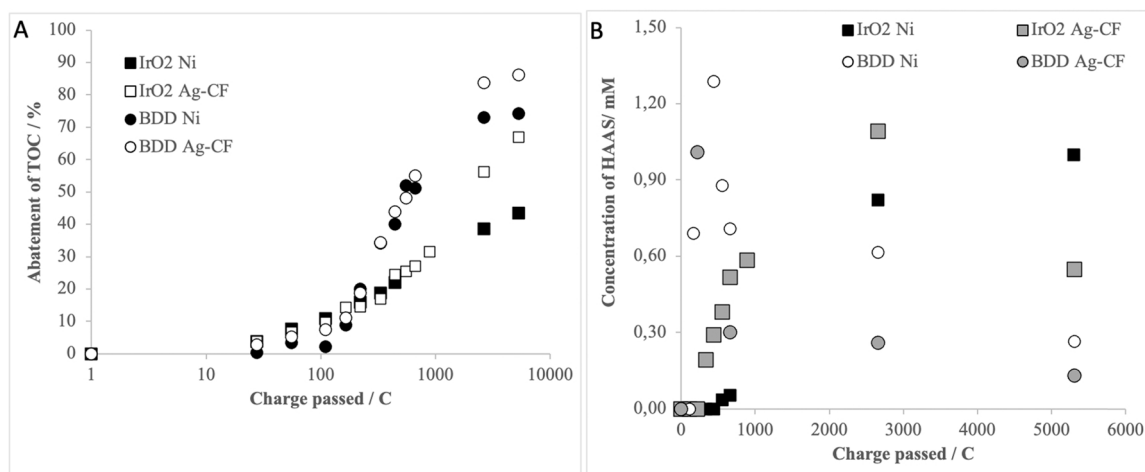


Fig. 17. Electrochemical treatment of water solutions of phenol (2 mM) and NaCl (0.5 M) under galvanostatic conditions in an undivided cell equipped with one (Ti/IrO₂-Ta₂O₅ or BDD) anode and two cathodes (Ag and carbon felt) at 10.3 mA cm⁻². (A) TOC abatement and (B) total concentrations of HAAs vs. electric charge. Adapted with permission from [218]. Copyright Elsevier B.V. 2021.

of seawater and brackish water) and in industrial plants (as an example, wastewater with different salinities), or produced using thermolytic solutions (regenerated with waste heat), can be potentially used to produce electric energy by reverse electrodialysis (RED), using stacks constituted by many pairs of anion and cation exchange membranes placed between the two electrodes and fed with two solutions with a large difference in salt concentrations [250–252]. In most of cases, the salinity gradient depends on differences in the NaCl concentration between the two solutions. The electromotive force for a stack assembly of *N* membrane pairs fed with aqueous solutions of NaCl can be estimated from Eq. (37) [250].

$$E = 2NpRT \ln(a_c/a_d)/F \quad (37)$$

where *R* is the gas constant, *T* the absolute temperature, *p* the average permselectivity of the membrane pair, *F* the Faraday constant and *a_c* and *a_d* the solute activities in concentrated and diluted solutions, respectively.

Quite recently, some scholars have proposed to use the electromotive force generated by the salinity gradients to achieve the treatment of wastewater contaminated by recalcitrant organics in RED stacks assembled with a relatively small number of membrane pairs and adequate electrodes, thus avoiding the use of electric energy necessary that is associated to conventional electrolysis [253–258]. In particular, it has been shown that it is possible to use river, seawater and/or brine solutions to treat various kinds of wastewater contaminated by organics in the anodic compartment by active chlorine generated at IrO₂-based anodes [254,255,259]. In some cases, the removal of organics was assisted in the cathodic compartment by EF process using carbonaceous cathodes and Fe(II) as catalyst (Fig. 18) [254].

The treatment of wastewater by electrogenerated active chlorine in RED stacks was performed both in lab-scale devices [253–257] and in a pilot plant [258]. It is worth to mention that the plants devoted to the treatment of industrial wastewater deal often with water characterized by different salinities; in this context, the group of Scialdone has proposed in 2020 the use of these salinity gradients and of a RED stack to partly decontaminate such wastewater, potentially allowing a huge saving of energy [251]. In particular, they have studied, in a first proof-of-concept evaluation, the case of two synthetic wastewater solutions with a TOC content of 120 mg L⁻¹ and very different NaCl contents close to those reported for industrial wastewater produced during oil exploitation activities. A large part of the wastewater with high NaCl (about 2/3) used to provide the salinity gradient was successfully treated, as shown in Fig. 19 [251].

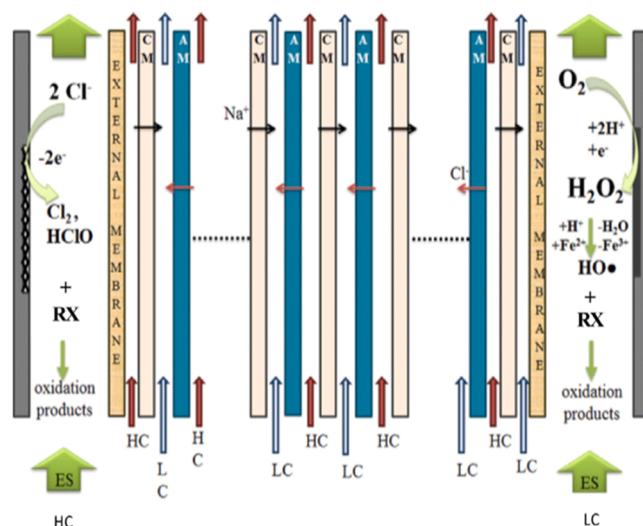


Fig. 18. Scheme of a RED stack showing cationic, anionic and external membranes, electrodes, the main reactions occurring in the electrode compartments, concentrated (HC), diluted (LC) and electrode solutions (ES) flowing in the stack and the ionic flux generated by the salt gradients. Anion-exchange membranes (AMs) and cation-exchange membranes (CMs) are used to selectively drive the flow of positive charge ions to the right (toward the cathode) and the negatively charged ions to the left (toward the anode). The flow of these charged ions is converted in a flow of electrons at the electrodes that sustain the electrogeneration of oxidants.

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However, the development of redox processes driven by salinity gradients is limited, in order to avoid using too large and expensive stacks, to cases where small cell potentials are required and large salinity gradients are available, thus not allowing exploiting the energy present in water with limited salinity gradients. Assisted reverse electrodialysis (A-RED), which couples the energy coming from salinity gradient with the external electric energy applied in the direction of the diffusional transport of ions that follows chemical potential gradients, can be used to solve this problem. Indeed, it was found that A-RED accelerates the removal of organics, allows the use of smaller salinity gradients than RED and requires less electrical energy as compared to electrolysis [260]. In addition, a simplified economic analysis, performed for the anodic treatment of a synthetic wastewater contaminated with formic

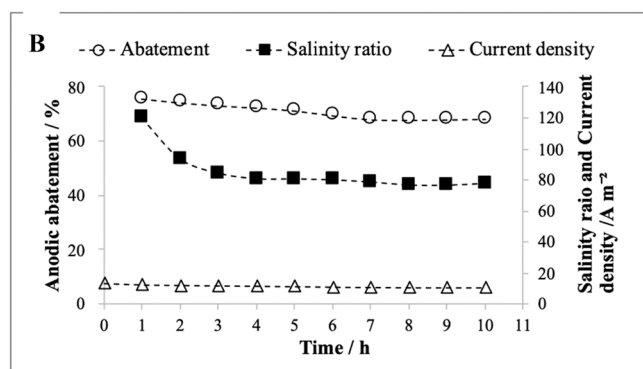


Fig. 19. Trend of TOC abatement in the anodic compartment, salinity ratio and current density vs. time. RED performed with HC (NaCl concentration 120 g L⁻¹) and LC (NaCl concentration 50 mg L⁻¹) fed to the stack (20 L each, flow rate: 260 mL min⁻¹) and, respectively, in the anode and cathode compartments (0.2 L each, flow rate: 200 mL min⁻¹). Number of membrane pairs: 60; cathode: carbon felt; anode: DSA (Ti/RuO₂-IrO₂). Adapted with permission from [251]. Copyright Elsevier B.V. 2020.

acid as model organic compound, has shown that A-RED can be less expensive than both electrolysis and RED [260]. However, until now, only preliminary results with synthetic wastewater were reported. Hence, in order to evaluate the potential of these approaches more studies are necessary, focusing on the utilization of real wastewater.

3.4. Advantages and disadvantages and key aspects to be addressed

Overall, the utilization of active chlorine generated at suitable electrocatalytic materials for the treatment of wastewater contaminated by organic pollutants presents some advantages as compared to direct chloride-free EO explained in Section 2: (i) the possibility to use cheaper electrodes; (ii) higher current efficiencies; and/or (iii) lower energy consumptions. Conversely, the utilization of electrogenerated active chlorine gives rise to a more difficult optimization of the operation conditions and to the potential formation of chlorinated byproducts. Therefore, if water contains chlorides, the potential formation of these compounds in the anodic compartment of the electrochemical cell has always to be conveniently addressed.

In addition, the electrochemical treatment of wastewater with active chlorine (using selected anodes and conditions) offers various advantages over the chemical treatment with chlorine derivatives, including the following: (i) a faster removal of organic pollutants; (ii) the avoidance of transportation, storage and handling of unstable and dangerous chemicals; (iii) the lower generation of toxic chlorinated byproducts; and (iv) in many cases, lower overall costs [1,32,225]. On the other hand, the utilization of more complex and less investigated reactors is necessary.

In the next years, scholars will need to continue to study the effect of operation parameters on the performance of the process to guarantee an effective removal of all organics including chlorinated intermediates under economically viable conditions. Within this framework, the utilization of both low current densities and adequate cathodes seems a very promising approach. In addition, the potential utilization of salinity gradients presented by different wastewater matrices should be fully exploited in order to reduce the energy consumptions, as well as to use the peaks of electric energy production in order to reduce the average energy consumption of the IEO process.

It is important to remark that stirred cells, either with a divided or undivided configuration, have been commonly implemented in most IEO studies, obtaining different achievements; however, as discussed in Section 2.3, the figures obtained using these apparatuses cannot be directly correlated with the results obtained from other types of reactors. Therefore, the use of electrochemical flow cells should be the correct

strategy to currently investigate IEO in combination with computational tools to simulate, model and describe the factors that affects the internal cell compartments and hydro-dynamic conditions, to do a competent prototype-evaluation. In addition, in the next years, subsequent studies should be carried out considering other organic pollutants in real water matrices, as a priority, focusing on the identification of active chlorine species and proposing innovative applications of IEO and avoiding screening investigations too much similar to those achieved so far.

4. From purely cathodic to coupled redox processes

Significant progress has been made in the last six years not only in the context of direct and mediated oxidation, as thoroughly reviewed in previous Sections 2 and 3, but also in cathodic processes and their combination with the former ones. In forthcoming subsections, the critical aspects of the most relevant processes within these two latter categories are identified, putting emphasis on their main advantages and disadvantages throughout the text.

Worth mentioning, water decontamination partially or totally based on cathodic processes has been historically underrated as compared to that based on anodic technologies, since the effectiveness was rather limited to a small number of plain cathodes able to electrocatalyze specific reduction reactions that eventually led to an incomplete transformation of the target organic contaminants. Luckily, the extraordinary growth of nanosciences and the increased interplay between electrochemical science and technology and materials science has led to the manufacture of nanosized electrocatalysts with much greater cathodic efficiency, as well as the development of nanoengineered cathodes that act as direct or indirect sources of highly oxidizing free radicals like SO₄^{•-} or [•]OH, among other examples described below. Strategies based on such extreme size reduction give rise to the so-called nano-remediation technologies, which show a better performance than conventional ones as revealed by the higher degradation rates attained [261].

Hereby, three approaches to cathodically-mediated degradation of organic pollutants are described: (i) direct reduction of the target molecules at the cathode surface; (ii) two-electron oxygen reduction reaction (ORR) for H₂O₂ electrogeneration; and (iii) monoelectronic persulfate reduction to SO₄^{•-}, which was not included in our past review, but here it appears as a new topic due to the growing attention paid to the SO₄^{•-}-mediated AOPs. From this information and that reported in Sections 2 and 3, the information on different anode/cathode combinations is conveniently updated. Process coupling constitutes the core of the section, as it was a smart option identified in our past review to increase the efficiency of water decontamination [1]. The activation strategies to convert H₂O₂ into [•]OH are particularly highlighted, since H₂O₂ electrosynthesis for decentralized water treatment has recently become a hot topic (see subsection 4.2).

Note that coupled processes are aimed to increase the current efficiency, as the reaction occurring at the counter electrode is no more a side or parasitic phenomenon but a value-added process. The coupling of reduction and oxidation processes, also co-called paired electrolysis, is feasible using a single-compartment cell, which is the most employed configuration for treating organic pollutants. Alternatively, a divided reactor can be used, placing the solution as the catholyte to be subsequently pumped to the anode compartment, or viceversa, in continuous operation mode. Regardless of the type of cell, the current efficiency of the integral treatment will be a mere addition of that resulting from the anodic and cathodic processes, assuming that the solution presents enough conductivity. However, the efficiency of each of these two electrode processes that occur simultaneously could be somehow lower or greater as compared to that of each corresponding uncoupled process, owing to synergism or antagonism phenomena underwent by the redox species and their intermediates at the surface of the electrodes or in the bulk solution in the coupled system.

In our past review [1], the key aspects of the cathodic and coupled

approaches had been individuated. In particular, in single ER, as also occurs in EO, there is a trade-off between high efficiency (i.e., long electrolysis and hence, costly in terms of time spent) and high effectiveness (i.e., rather inefficient electrolysis and hence, costly due to the energy waste). Bright perspectives had then been forecast if the research could be focused on the following topics: (i) the development of new cathodes for ER; (ii) the innovation in reactors, as for example micro-reactors, which allow self-sustaining the Fenton-based processes with the anodic O_2 ; (iii) process modeling and simulation to support the scale-up; (iv) a detailed analysis of reaction byproducts to avoid the accumulation of toxic compounds; and (v) the powering with renewable energy in order to increase the viability of the electrochemical technologies under debate. As will be noticed in paragraphs below, most of this work has been addressed, and additional aspects of interest have emerged in the last six years.

4.1. Direct reduction

4.1.1. Purely cathodic process

Before addressing the direct reduction, it is necessary to include a brief prelude on the mediated reduction of the target pollutants in the catholyte, a process also described in a previous review [1]. It involves the generation of the reduced form of a redox mediator (Med) as exemplified in reaction (38), being subsequently reoxidized upon concomitant reduction of the pollutant in the bulk. Mediated electro-reduction (ER) is particularly well-suited for treating halocompounds, although even in such case the process efficiency is rather modest in aqueous medium due to the parasitic water oxidation by the redox mediator. Recently, the coupling of mediated ER and mediated electrooxidation (EO) to simultaneously degrade volatile organic compounds (VOCs) in the two compartments of a divided cell has been reported [262]. The $Med^{\bullet-}$ species was employed to reduce dichloromethane to ethanol in the catholyte, whereas the oxidized form of the mediator, generated from reaction (39), could oxidize phenol up to CO_2 in the anolyte.



As shown in Fig. 20, cobalt species like $[Co(CN)_5]^{3-}$ and $CoSO_4$ served as precursors (i.e., precatalysts) of $Co(I)$ and $Co(III)$ following reactions (38) and (39) in the catholyte and anolyte, respectively. The coupled ER-EO allowed utilizing the full cell, thus maximizing the Faradaic efficiency to manage two different contaminants. A screening of electrode materials for the ER and EO of the Co species revealed the

superiority of Ag over Ti and Cu as the cathode, and that of Pt over graphite and DSA as the anode. More sophisticated redox mediators such as coordination complexes have also been tested for reductive dehalogenation. Of particular interest are those formed between $Ni(I)$ or $Co(II)$ and ligands like (1,4,8,11-tetraazacyclotetradecane) (i.e., cyclam) or N,N' -bis(salicylidene)ethylenediamine (i.e., salen). Among them, $Ni(I)$ (cyclam) derivatives were proven to be very effective to reduce various molecules like bromoacetic or epichlorohydrin in water or hydroalcoholic mixtures [263], whereas $Co(II)$ (salen) immobilized on a 3D porous electrode was electroreduced to $Co(I)$ (salen) to allow the complete reduction of alachlor pesticide. Upon immobilization, the turnover number (TON) reached 360, as compared to 4 when the dissolved complex was employed [264]. Of note, the monoelectronic transformation of the $Co(II)$ to the $Co(I)$ complex requires 400 mV less than that of the Ni complexes.

The redox-mediated ER described above differs from direct reduction of the pollutant at the cathode surface, which includes both direct electron transfer (DET) to the adsorbed organic molecule and reduction mediated by powerful reductants (i.e., electron shuttles) electro-generated in situ, as for example adsorbed atomic hydrogen (H_{ads} or H^*). The latter option is clearly distinguished from the indirect reduction mentioned above, which was based on the use of redox mediators and, in some cases, it requires the adsorption of the pollutant on the cathode surface. A limited number of direct reduction cases has been reported since our previous review, especially if compared with purely anodic ones, but it is worth describing the most significant advances.

Obviously, the cathode composition determines the selectivity because it may either electrocatalyse or inhibit specific reactions. In particular, for many materials, cathodic reduction in aqueous streams shows concurrent H_2 evolution reaction (HER) at low overpotential, which drastically diminishes the Faradaic efficiency. An accurate control of the reduction reactions is only feasible upon smart modulation of the applied cathodic potential (E_{cath}), although in practice the electrolysis is usually made at constant current in order to speed up the decontamination process, at the expense of the current efficiency as parasitic reactions become uncontrolled. A wide range of products can be formed from ER for every single target pollutant because, at a given E_{cath} , the reduction routes may depend on the solution pH and the cathode nature. On the other hand, progressive nanosizing of the active surfaces has led to greater ER yields as compared to those obtained with conventional planar cathodes. (Bi)metallic and carbonaceous substrates are the most widely employed materials, although a progressive shift towards the use of carbon-supported metallic particles has been evidenced, which can be accounted for by three main reasons: (i) The exposure of a greater area to the reactants, which induces a higher

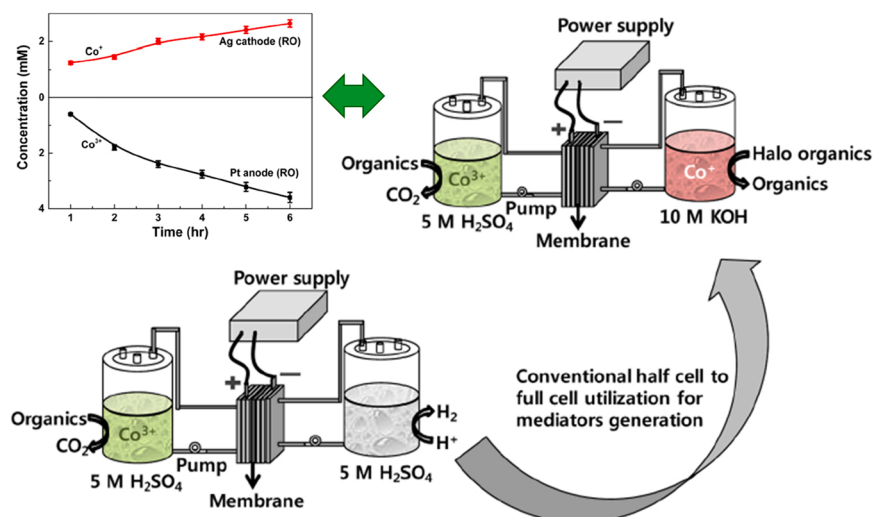


Fig. 20. The conventional mediated EO ($Co(III)$ as redox mediator), which only allows the degradation of an organic pollutant in the anolyte, is upgraded to a coupled ER-EO system that combines the previous degradation mode with the simultaneous $Co(I)$ -mediated degradation of an halocompound in the catholyte. The concentration vs. time plot illustrates the evolution of the reduced and oxidized forms of the redox mediator using an Ag cathode and a Pt anode in the divided cell.

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electroactivity; (ii) the enhancement of the noble metal-support interaction, with direct impact on surface catalysis [11]; and (iii) the greater metal dispersion (i.e., smaller agglomeration) that allows reducing its loading, which becomes a key factor when dealing with noble and semi-noble metals. For metal-loaded carbons, the loading is a critical parameter with large influence on the electroactivity, since it determines the number of truly exposed active sites.

Although direct ER is a very versatile tool to manage organic pollutants with varied structures, the most typically studied target molecules are azo dyes, nitrocompounds and halocompounds. Among the latter, the organochlorine byproducts (e.g., THMs, HAAs) generated during the IEO process have special relevance (see Section 3). Successful detoxification of the aqueous streams can be achieved in all these cases at a relatively low energy consumption (i.e., only a quick partial conversion is aimed), unless more toxic byproducts like certain amines are accumulated. New advances for the ER of dye solutions have not been reported in the last lustrum. Nitro compounds, as also occurs with other oxygenated organic nitrogen substrates like oximes and nitrones, are very prone to ER, mainly leading to the formation of hydroxylamines that can be further reduced to amines at sufficiently negative E_{cath} . This was verified for the nitroimidazole antibiotic dimetridazole [265]. However, the conjunction of hydroxylated and dehydroxylated amines should be avoided, since it yields azo and azoxy derivatives that decrease the biodegradability of the treated effluent [366]. Nitroso compounds can also be obtained as products, but only when certain cathodes are employed because they are more reactive than the parent nitro molecules [267].

Much greater progress has been made in the development of reductive processes for the cleavage of the C-X bond (where X = F, Cl, Br, I), giving rise to the so-called electroreductive dehalogenation. One of most interesting features is that, unlike oxidative dehalogenation discussed in previous sections, there are no concerns related to the accumulation of persistent and toxic oxychlorine anions (i.e., ClO_3^- and ClO_4^-) if the cell configuration and/or the anode nature are thoughtfully chosen, which is advantageous because the resulting higher biodegradability allows the coupling with cheaper biological post-treatment [266]. Mechanistically, the ER treatment applied to halogenated organic pollutants (i.e., organic halides) can occur via direct reduction (through a concerted or a step-wise mechanism to reach C-X bond cleavage) [268] or be mediated by atomic hydrogen [1] (i.e., electrocatalytic hydrodehalogenation, also known as electrocatalytic hydrogenolysis (ECH)). Metals like Ag or Cu, either in massive form or as carbon-supported metal particles, are excellent to promote the former route, whereas noble metals like Pd favor the formation of H_{ads} ($E^0 = -2.1$ V vs. reversible hydrogen electrode (RHE)) that further induces the ECH process (see below) [269]. Note that the ECH process is affected by pH, since it modifies the amount of H_{ads} . In addition, in both mechanisms the pH modification may alter the pollutant structure and hence, its adsorption. Overall, the chemistry involved in dehalogenation via DET is simpler than that leading to the reductive transformation of N-O bonds, which can yield complex product mixtures (see above) [267].

There is a close relationship between the properties of the electrocatalyst (structure, morphology, chemical composition, size and conformation) and its performance and stability [270]. In the case of silver, the best material for DET, specific surface interactions with the C-X bond boost the electron transfer, eventually accelerating the dehalogenation even for polyhalogenated molecules, as discussed by experts in the field like Rondinini [1]. The great affinity of the Ag surface for halides favors the weakening of the C-X bond present in the adsorbed organic halide [271]. In general, electrode size reduction from massive to micro- and nanostructured ones is beneficial, with nanosized Ag yielding better results thanks to the greater number of active sites [270]. This has been shown in a fundamental study in which quasi-spherical (i.e., polyoriented) Ag nanoparticles (NPs) of different sizes from 6 to 50 nm were employed to dechlorinate trichloromethane [272]. To carry out bulk electrolysis, Ag NPs have to be supported, preferentially in 3D

substrates like Ni foam [273]. In the case of gaseous organic halides, Ag-modified gas-diffusion electrodes (GDEs) become a better alternative, as demonstrated for trichloromethane employing a silver-coated Ni net as support coated with a Vulcan XC72R carbon + PTFE + Ag NPs mixture [271]. The GDE (100 cm^2) was inserted in a two-compartment filter-press cell equipped with a Nafion 117 cation exchange membrane (Fig. 21a), being quite effective to produce methane since the measured $\text{Cl}^-/\text{CHCl}_3$ ratio was 2.81. Multimetallic cathodes that include Ag are also an option to further improve the ER performance. It is also worthwhile to highlight that Cu and its alloys and oxides offer another good choice for dehalogenation, since it is a cheap and eco-friendly metal that is not classified as a critical raw material. In particular, Cu-catalyzed arylation converts halogenated aromatic compounds into non-halogenated derivatives like phenols upon nucleophilic substitution by OH^- . This is especially effective for iodinated and some brominated molecules, whereas aryl chlorides show a more limited reactivity that depends on the substituents [274].

On the other hand, hydrodehalogenation or ECH was first developed to get rid of the halogens used as protective groups in organic synthesis, although lately it has found a new application as a simple and efficient method for the treatment of halogenated water pollutants at low concentrations. Among noble metals for ECH, Pd is superior to Ru, Rh and Pt thanks to its higher ability to intercalate hydrogen in its lattice, which is a source of H_{ads} [268]. Nonetheless, noble-metal-based ECH must be carefully managed, since unwanted species like adsorbed hydrogen (H_{ads}) and molecular H_2 can be formed if E_{cath} is not selected with accuracy, which decreases the efficiency and may induce fragility in the metal.

Furthermore, as a drawback to be noticed, noble catalysts suffer from progressive deactivation [274]. Electrocatalytic dehalogenation has been mainly performed with Pd-based cathodes fabricated via different methods [270]. For instance, 2,4-dichlorophenol hydrodechlorination was achieved using Pd NPs [275]. The importance of the presence of charged groups in the treated molecule was revealed by the authors, concluding that deprotonation yielding negatively-charged species

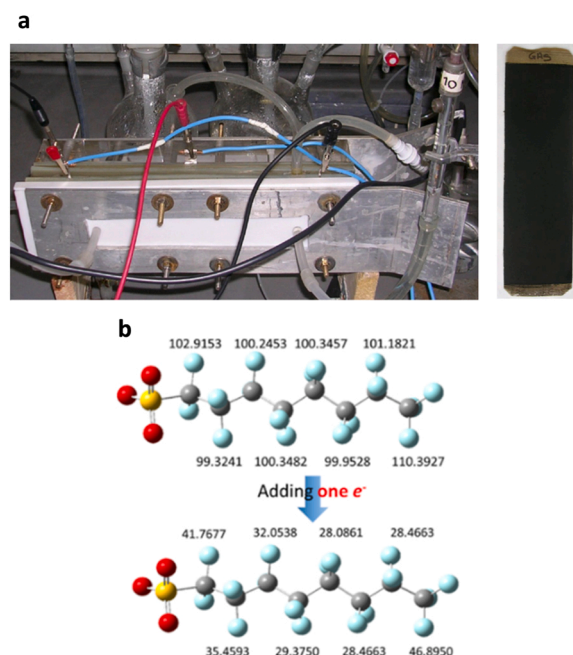


Fig. 21. (a) Divided filter-press cell (left) equipped with an Ag-loaded GDE (100 cm^2 right) to transform CHCl_3 into CH_4 by ER process. (b) Reduction of the C-F bond dissociation free energy as one electron is transferred from the cathode to the PFOS molecule during ER treatment.

(a) Adapted with permission from [271]. Copyright 2021 Wiley-VCH GmbH. (b) Adapted with permission from [280]. Copyright 2019 ACS.

induces repulsion by the cathode and eventually diminishes the dehalogenation efficiency. In order to favor the reactivity between the organic halides and H^* , the use of foams as supports has become trend. Hence, the antimicrobial triclosan was completely dechlorinated to 2-phenoxyphenol using a Cu foam coated with Pd-loaded N-doped graphene, which allowed a halogen removal rate 5.5-fold higher than that attained with a Pd-loaded Cu foam [276]. The authors did not observe any Pd or Cu leaching from the cathodes, and H^* was identified by means of ESR. A Pd-loaded Ni foam led to the quickest *p*-chloronitrobenzene dechlorination, being complete after 30 min at 10 mA cm^{-2} , as compared to Ni foam or Ti|Pd cathodes. Aniline was the only product detected [277]. Multi-walled carbon nanotubes (MWCNTs) are another good alternative as 3D supports to load Pd NPs. This was evidenced for 4-chlorophenol hydrodechlorination in a particle reactor in which Ti plates were employed as the electrodes and the Pd/MWCNTs particles were suspended in between. Complete dechlorination was reached at 30 min when the particle size was 6.4 nm, whereas size increase up to 13.1 nm negatively affected the dehalogenation process [278].

If compared with electrochemical dechlorination, deiodination has been much less investigated, despite the fact that iodine-containing contrast media used in medicine account for a substantial percentage of toxic waste generated in the health sector. In contrast to existing knowledge on dechlorination and debromination, the unexpected production of active halogen species (i.e., active iodine) during the treatment has been suggested [279]. Worth mentioning, the recovery of the halogenated species in their ionic form can be performed in dehalogenation processes, which is especially interesting for iodine compounds [266].

From a thermodynamics perspective, the cleavage of the C-F bond is extremely difficult as compared to the previous examples, as a result of its high enthalpy (i.e., 566 kJ mol^{-1}). This explains why DET has not been reported for (C-F)-containing pollutants [269]. Nonetheless, the UV-assisted electro-reductive defluorination of perfluorooctane sulfonate (PFOS), highly refractory to bioremediation and advanced oxidation, is a first example of electrochemically-mediated C-F bond cleavage for perfluoroalkylated substances (PFAS). Perfluoroalkyl acids were identified as byproducts when using a cathode coated with COOH-functionalized carbon nanotubes (CNTs) [280]. From density functional theory (DFT) calculations, it has been demonstrated that a monoelectronic transfer to the target fluorinated pollutant during the ER process has strong positive impact, as it decreases the average dissociation free energy of the C-F bond from ~ 102 to $\sim 30 \text{ kcal mol}^{-1}$, as can be observed in Fig. 21b. On the other hand, a Rh-catalyzed Ni foam behaved better than cathodes prepared with any other noble metal catalyst and 3D support for the electrocatalytic hydrodefluorination of 18 fluoroaromatic molecules under mild conditions, transforming all the F atoms into F^- [281]. This work also proves that the theoretical or computational studies for interpreting the experimental results from anodic or cathodic processes can be considered a powerful tool to elucidate the mechanisms from a molecular point of view (see Section 2.2.3).

Retro-dihalogenation, a method derived from dihalogenation reactions with importance in organic synthesis, represents a novel approach to the problem described in this subsection. This is based on the dehalogenation of organic pollutants in the presence of simple alkene acceptors. The strategy has been demonstrated for lindane and other organic halides, and involves two consecutive steps [282]: (i) the cathodic dehalogenation, yielding the halide anions (X^-); and (ii) the simultaneous anodic oxidation of X^- in the presence of an alkene, whose halogenation gives rise to value-added organic dihalides. A larger-scale degradation of lindane using graphite electrodes at 4 mA cm^{-2} yielded benzene (> 95%).

As a final remark, polymerization, poisoning, swelling and passivation phenomena appearing during direct ER may cause the deactivation of the electrocatalyst, negatively affecting the process performance [283]. Therefore, more efforts should be paid to the development of

re-activation procedures and their follow-up upon implementation in prolonged electrolytic trials.

4.1.2. Coupling with anodic processes

In our past review, several cases of coupling between direct reduction (i.e., DET or H^* -mediated) and direct or mediated oxidation had been presented [1]. Paired electrochemical reactions can be a means to maximize the current efficiency, as has been well explored in organic synthesis [284]. In environmental electrochemistry, the viability and appropriateness of this type of technology depends on the composition of the contaminated effluent, being suitable for the treatment of: (i) mixtures of electroactive organic compounds exhibiting functional groups with different tendency towards DET to/from the electrode surface; (ii) organic pollutants that can be either reduced or oxidized and hence, setups with convenient cathodes and anodes that allow the simultaneous degradation eventually accelerate the decontamination; and (iii) organic pollutants that lead to the formation of byproducts upon either cathodic or anodic reaction, these being unable to undergo subsequent transformations at the same electrode.

A scarce number of publications on this subject has appeared since 2015. A good example is the degradation of model solutions of 500 mL of 2-nitrotoluene via sequential ER-EO coupling (each single treatment performed for 120 min), using a divided electrochemical cell equipped with a Ti cathode, a DSA anode and a cationic exchange membrane. In single ER, the cathodic H^* production allowed a 95% of pollutant removal and led to the formation of 2-toluidine, whereas the EO only caused a concentration decay of 10% [285]. However, single ER only caused a mineralization of 5%, much lower than 40% achieved by ER-EO. Based on these results, the authors showed that the ER-EO process was superior to single ER and EO for the decontamination of actual wastewater containing nitroaromatic compounds.

In agreement with new trends in electrocatalysis, single atom catalysts (SACs) can be employed as relatively cheap and highly efficient materials. Some authors focused on the role of the Co-SAC loaded in a sulphide graphene cathode as a source of H^* and H_2O_2 to promote the hydrodechlorination of 2,4-dichlorobenzoic acid in a 450-mL divided cell [286]. However, the generation of Cl_2 at the DSA anode suggests that their system actually behaved as an ER-EO system because this oxidant can diffuse through the membrane. As a result, the pollutant concentration decay was higher than 91% at 50 mA cm^{-2} , which was accompanied by 80% TOC abatement.

4.2. Oxygen reduction to hydrogen peroxide

4.2.1. H_2O_2 electrosynthesis

The H_2O_2 market has experienced an unceasing growth in recent years, accounting for \$4.8 billion in 2019 and expecting a registered compound annual growth rate over 5.7% within the period 2020–2026 [287]. These numbers arise from an annual production that exceeds 3 million tons and may reach 5.2 million tons per year by 2020 [228]. Currently, H_2O_2 is applied as oxidant, disinfectant and bleaching agent. The two main drivers are industrial pulp bleaching and catalytic epoxidation, such as propylene oxide (PO) synthesis from propylene, since chlorine, chlorohydrin and hydroperoxides have been gradually replaced as oxidants in the pulp and paper sector and in the so-called hydrogen peroxide PO production (i.e., HPPO process [288]). Since its first isolation in 1818 [48], H_2O_2 has become a value-added and eco-friendly commodity that fits perfectly in a wide range of applications. The quest for alternative H_2O_2 synthesis routes to the governing but reagent-, temperature- and solvent-dependent anthraquinone oxidation process, as well as to direct catalysis of the reaction between H_2 and O_2 , offers great opportunities to benign electrochemical approaches. Through electrosynthesis, issues like dangerous transportation and plant footprint due to storage and manipulation are avoided. Furthermore, there is a growing need of decentralized systems that allow the point-of-use H_2O_2 generation able to reach concentrations

on demand, thus adapting the treatment to the varying conditions of the effluents. In addition, in situ H_2O_2 electrosynthesis adds versatility in niche applications that range from fruit processing to cooling towers, since small to medium-size, compact and modular units can serve to easily modulate the electrolysis conditions and assure the desired water quality in terms of disinfection. Such bright perspectives have resulted in a new awakening of H_2O_2 electrosynthesis [289,290], as confirmed from the flourishing of companies that currently commercialize H_2O_2 electrogenerators, which is the case of the start-up HPNow. Moreover, in the wastewater treatment segment, the H_2O_2 -based electrochemical advanced oxidation process (EAOPs, subsections 4.2.1–4.2.3) are also envisaged to generate revenue gains in the near future.

The current dependence of H_2O_2 -based processes on the commercially available reagent can be addressed by means of its in situ electrochemical production, which is achievable through either anodic or cathodic routes. Although the anodic H_2O_2 electrosynthesis from two-electron water oxidation (reaction (40), $E^0 = 1.760 \text{ V vs. SHE}$) is feasible [291], it has not been as widely explored as the cathodic route within the context of the treatment of organic pollutants in aqueous media because of its lower interest, as it does not allow the smart coupling with EO processes reviewed in preliminary sections. Moreover, the anodic route shows a large overpotential and low production rates unless interfacial engineering that promotes local O_2 confinement is put into practice [292].



This subsection critically discusses the innovations on electrode materials and reactors for cathodic H_2O_2 electrosynthesis based on the two-electron oxygen reduction reaction (ORR), lately emerged as a very hot topic. Actually, this should be better considered a rebirth because the process itself is known since many years ago [293]. The ORR to H_2O_2 is more favorable in acidic medium (reaction (41), $E^0 = 0.695 \text{ V vs. SHE}$), since under alkaline conditions the four-electron ORR to water prevails [48].



4.2.2. Unmodified cathode materials

Reaction (41) proceeds via two consecutive monoprotonic/mono-electronic cathodic reactions, with OOH^* (i.e., OOH_{ads}) as crucial intermediate. Among the cathode materials for two-electron ORR, carbon is the gold standard, especially in the field of water treatment, owing to its abundance and excellent properties like high durability, electrical conductivity and activity towards reaction (41), also fulfilling the low cost demanded in the water treatment sector because of this is still a low value-added activity. Graphite and glassy carbon were the first carbonaceous substrates tested to investigate the ORR. However, planar cathodes tend to show a sluggish kinetics that ends in low current efficiencies, which impedes the penetration of the technology into the market. Aiming to solve this problem, three different types of carbons with a larger electroactive surface area have been employed by researchers and technologists: (i) beds of carbon particles; (ii) three-dimensional (i.e., porous) fabrics like carbon felt or reticulated vitreous carbon (RVC); and (iii) nanosized materials such as graphene in its various forms, nanotubes and nanofibers, supported on various substrates. Another option, bridging the two latter types, is constituted by nanoengineered 3D materials like nanostructured mesoporous carbon [261]. The ORR to H_2O_2 in an FM01-LC filter-press cell was comparatively performed with BDD, carbon felt and RVC cathodes, evidencing that the potential ranges for ORR under mass transport control were different for each material, with a greater i_{lim} for carbon felt due to its larger volumetric area [294]. More details on carbonaceous materials for H_2O_2 production can be found in some recent comprehensive reviews [295,296]. Additionally, the latest works put emphasis on the

development of carbon-supported electrocatalysts that favor reaction (41), as explained below in this subsection.

The electrochemical characterization of a given carbon or carbon-supported electrocatalyst is one of the requirements to assess its selectivity in H_2O_2 electrosynthesis, being this crucial parameter sometimes misunderstood or creating confusion among readers. Rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) measurements inform about the H_2O_2 molar fraction selectivity, whereas bulk electrolysis yields Faradaic efficiency selectivity data as calculated from accumulated H_2O_2 concentration. Considering a benchmark Faradaic efficiency selectivity of 82% for the investigated electrocatalyst, the result obtained for RRDE selectivity is 90%, being the former calculation more informative [297].

With the aforementioned carbons, two great types of cell configurations have been devised to carry out quantitative electrolytic trials. The first one involves the use of an immersed cathode that receives dissolved oxygen from sparged air or pure O_2 . As a major shortcoming, the low O_2 solubility in water ($\sim 8 \text{ mg L}^{-1}$ when air at atmospheric pressure and 25°C is employed, which is the most typical situation) limits the H_2O_2 productivity [1]. There exist several possibilities to solve this handicap, as will be commented below. One of them represents a radical change, since it consists in using a GDE, in which gaseous O_2 or air is fed from an air pump or compressor through an air chamber and a gas diffusion layer (GDL) to reach a hydrophobized catalytic layer (CL) in contact with the solution. Carbon cloth and carbon paper are the most usual substrates, acting as GDL at the same time, but some authors replace the GDL-CL ensemble by a conductive catalytic layer (CCL) composed of a metallic mesh coated with a carbon + polymer mixture [298]. GDEs are the benchmark cathodes for H_2O_2 electrosynthesis because of the comparatively higher O_2 utilization efficiency, mass production rates and cost-effectiveness [299]. This good behavior arises from the three phase interface or three phase boundary (TPB) formed when the diffusion layer is coated with the carbon + polymer mixture [300], which provides simultaneous access to the electrons (through the conductive carbon), the O_2 gas (flowing freely through the hydrophobizing polymer) and the aqueous electrolyte (wetting the catalytic layer and favoring the dissolution of the reduction product). Much effort has been put to further optimize their performance, and techno-economic evaluation of H_2O_2 electrosynthesis with a GDE (9 cm^2) operating for $\sim 1000 \text{ h}$ has been recently performed by Wang and co-workers, demonstrating that it is a competitive technology [301]. The current efficiency ($\sim 85\%$) and energy consumption ($< 10 \text{ kWh (kg H}_2\text{O}_2)^{-1}$) were quite constant, yielding an overall cost of $0.88 \$ (\text{kg H}_2\text{O}_2)^{-1}$. A similar efficiency ($\sim 88\%$) and energy consumption ($< 12 \text{ kWh (kg H}_2\text{O}_2)^{-1}$) were reported by Ding et al. [302] with a divided flow cell. The use of a ceramic membrane instead of a conventional polymer membrane allowed keeping the cell voltage around a moderate value. With the goal of obtaining a higher production of H_2O_2 , a stacked electrochemical reactor equipped with GDEs as the cathodes and DSA plates as the anodes was operated in continuous mode [303]. The authors found that the use of three electrode pairs enhanced the mass production rate from 44 to $220 \text{ mg L}^{-1} \text{ min}^{-1}$ when the interelectrode distance was decreased from 5 to 1 mm . Additionally, the H_2O_2 concentration was 7-fold greater when increasing the number of electrode pairs from 1 to 9 . Under optimized conditions, the H_2O_2 production rate was higher than those previously reached with other systems, and a maximum of $1929 \text{ mg L}^{-1} \text{ min}^{-1}$ was attained. Worth noticing, the applied current (I_{appl}) or E_{cath} , the electrolyte composition, the number of electrolyte compartments, the electrode area-to-volume ratio and the residence time are highly influential operational parameters that affect the H_2O_2 productivity and have been investigated in the large set of articles published in recent years. In an undivided cell, which is the most widespread setup to operate the H_2O_2 -based EAOPs for water treatment, the H_2O_2 concentration that can be effectively accumulated is limited by its partial anodic oxidation to O_2 . However, the presence of organic molecules minimizes such destruction if they are preferentially oxidized,

eventually enhancing the H_2O_2 production [304].

Several strategies have been followed in recent years to enhance the H_2O_2 production when an immersed carbonaceous material or a GDE are employed as the cathode. In the former case, a GDE-like immersed 3D cathode was constructed with a graphite felt piece on top of carbon cloth, which was fed with air pumped through an air chamber. The cathode was implemented in a filter-press cell and produced H_2O_2 with a current efficiency close to 100% at short time thanks to the enhanced mass transport of hydronium ions [305].

4.2.3. Carbon hydrophobization

A second strategy relies on hydrophobization, which has been performed by some scholars to confer waterproofing that creates a sort of TPB, thus mimicking the classical manufacture of GDEs but still using sparged O_2 or air. A PTFE-based damp-proof coating serve to increase the H_2O_2 concentration up to 677.5 mg L^{-1} (i.e., $54.2 \text{ mg cm}^{-2} \text{ h}^{-1}$ and current efficiency of 79%), which was attributed to the lower wetting and the consequently larger ability of the modified acetylene black powder to utilize both, the dissolved O_2 and the O_2 bubbles [306]. Similarly, a graphite + PTFE mixture coated on a stainless steel mesh and provided with an external PTFE film showed a greater current efficiency as compared with the cathode without the external hydrophobic film (i.e., 74% vs. 57%) [307]. This kind of manufacture is aimed at endowing the cathode with a specific hydrophilic-hydrophobic balance, so that the O_2 utilization is maximized thanks to its confinement and facilitated diffusion towards the active sites. The obtained materials exhibit an asymmetric wettability and are called Janus structures. As can be seen in Fig. 22a, totally and partially wet pores of the carbon felt cathode coexist in such state. This potentially favors the simultaneous reduction of dissolved and gaseous O_2 , although some authors have reported an enhanced but similar behavior of the hydrophobic, hydrophilic and Janus structures [308]. In contrast, the superiority of the Janus cathode, prepared with a carbon felt coated with a mixture of

oxidized carbon black and poly(vinylidene fluoride) (PVDF), in terms of H_2O_2 concentration and O_2 utilization efficiency was clearly evidenced by others when pure O_2 was sparged at 6 mL min^{-1} , as depicted in Figs. 22b and 22c [309]. The extreme case in the hydrophobization strategy gives rise to the so-called superhydrophobic cathodes, with correspondingly high contact angles (Fig. 22d). The resulting natural air-diffusion electrode (NADE) enhances the O_2 diffusion by 5.7-fold as compared to conventional GDEs [310], a feature that allows the use of atmospheric air for H_2O_2 production if the cathode is properly placed in the cell (Fig. 22e). Similar so-called supraerophilic cathodes, with great ability to adsorb O_2 microbubbles and minimize the H_2O_2 reduction, have been prepared for H_2O_2 electrosynthesis [311]. Further comments on the open possibilities derived from these extreme cases are given below.

The improvement of the H_2O_2 production rate when using GDEs can also be achieved by means of optimum hydrophobization. PTFE is the most widely used agent to confer hydrophobic characteristics to the CL, thus preventing excessive wetting of the pores that would impede the O_2 diffusion towards the active sites, as well as flooding of the air chamber. Waterproof management is thus an essential task when working with GDEs. Some researchers employed alternative polymers like PVDF [310], whereas others preferred a silicon like polydimethylsiloxane (PDMS) as a less expensive polymer to trap more O_2 molecules, accelerate their transport and reduce the water flooding [312]. Commercial ion-conducting polymers (i.e., ionomers) like Nafion have also been used [313], but they are based on PTFE, which causes mass transport losses; novel ionomers based on perfluoro(2-methylene-4-methyl-1,3-dioxolane) (PFMMD) induce a greater gas permeability [314]. Indeed, cathode architectures based on catalyst/ionomer bulk heterojunctions are expected to provide a substantial amelioration in terms of H_2O_2 production efficiency, as recently proven for the electrochemical CO_2 reduction reaction (CO_2RR) [315]. The resulting heterojunction structure is able to extend gas and ion transport to the micrometer scale

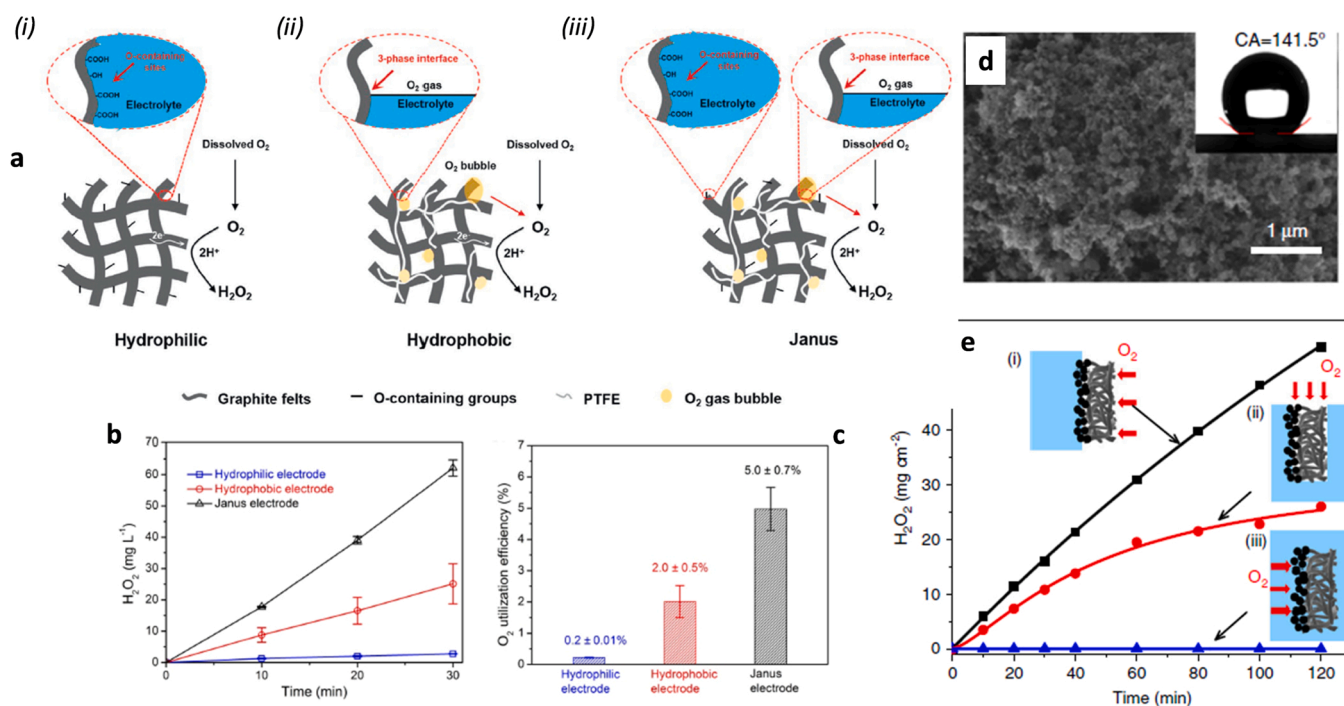


Fig. 22. (a) Mechanisms for H_2O_2 generation at hydrophilic (i), hydrophobic (ii) and Janus (iii) carbon felts. (b) H_2O_2 production vs. electrolysis time and (c) O_2 utilization efficiencies at 30 min for the Janus, hydrophobic, and hydrophilic electrodes at -0.4 V vs. Ag/AgCl with O_2 sparged at 6 mL min^{-1} . (d) SEM image of catalytic layer and contact angle of a NADE prepared with a PTFE/carbon black ratio of 1.5, and (e) H_2O_2 production at 60 mA cm^{-2} with the same cathode place in different positions.

(a) Adapted with permission from [308]. Copyright 2021 Elsevier. (b) Adapted with permission from [309]. Copyright 2020 ACS. (c) Adapted with permission from [310]. Copyright 2020 Nature Publ. Group.

thanks to the balanced hydrophobicity/hydrophilicity of the polymer. The GDE structure is schematized in Fig. 23a. In the absence of the ionomer, the lack of enough O_2 at the catalytic sites induces the occurrence of competing reactions, like HER (Fig. 23b), which decreases the ORR efficiency. In contrast, the ionomer favors the decoupled gas transport (through its hydrophobic domains) and water uptake and ion transport (through its hydrophilic domains), as illustrated in Fig. 23c. The modeled O_2 availability at the catalyst surface in both cases is depicted in Figs. 23d and 23e. Another relatively new strategy is based on the so-called polymers of intrinsic microporosity (PIMs), which may induce a greater storage of O_2 because of their large internal surface area and ability to bind gases [316]; hence, it can be hypothesized that their mixing with carbons would stimulate the triphasic interfacial reactivity to enhance the two-electron ORR, as deduced from four-electron O_2 reduction tested upon direct deposition of PIMs on working Pt electrodes [317]. A final interesting option to be further explored in the future, since it has only been tested in microbial fuel cells so far, consists in the use of a waterproof breathable membrane (WBM) as DL with improved air permeability, coated with the CL and attached to a stainless steel substrate [312].

4.2.4. Reactor design

A different strategy to enhance the H_2O_2 production focuses on the reactor design, for example with goal of enhancing the mass transport of

dissolved O_2 to the cathode surface. Conventional stirred tank reactors with immersed carbonaceous cathodes show a limited transport, ending in relatively low H_2O_2 concentrations. The introduction of turbulence promoters in this type of reactor or in flow cells could improve the process. The group of Bisang employed a rotating cylinder electrode (RCE), which has been previously shown very successful for metal recovery. The RCE, made of RVC or carbon felt supported on graphite, served as the cathode to boost the O_2 (0.1 MPa) convection in an undivided [318] and divided [319] cell. A concentration as high as 8.4 g L^{-1} H_2O_2 was achieved after 6 h using RVC in a 0.5 M NaOH solution at 40 mA cm^{-2} and rotation speed of 1000 rpm, with current efficiency of 79%. This good result opens the door to future studies with an RCE cell, which is easily adaptable to work in continuous mode once the residence time is optimized. Microfluidic reactors with an optimum interelectrode distance in the range of few hundreds of micrometers, was first proposed Scialdone for the degradation of organic halides [241, 242]. The device promoted the two-electron ORR at a cheap graphite plate in flow-by mode, showing a superior performance as compared to a conventional macroreactor [242]. This is highly beneficial for practical application because graphite has lower cost and higher durability than other carbons throughout this subsection. More recently, several microreactors connected in series allowed the degradation of Acid Orange 7 azo dye upon in situ electrogeneration of H_2O_2 in continuous mode [194]. Note that the reactors for H_2O_2 production are operated at constant current (or constant E_{cath}), but it has been recently suggested that pulsed current electrolysis might induce a 62% greater accumulation of the oxidant thanks to the minimization of its reduction at the RVC foam cathode [320].

Smart reactor design and optimization of operation conditions has also been carried out for ORR with GDEs. A tubular GDE made of self-standing MWCNTs (length of 44 cm, outer diameter of $\sim 1.7 \text{ mm}$ and wall thickness of $275 \mu\text{m}$) was manufactured from a microfiltration hollow fiber membrane. Unlike typical GDEs, the O_2 was fed through the inner part of the tube. Although the H_2O_2 production was higher than that attained using dissolved O_2 , more investigation is needed because the current efficiency was lower than 50% [321].

4.2.5. Self-sustained H_2O_2 production

In the fields of electrochemical H_2O_2 production and the H_2O_2 -based EAOPs, one of the most remarkable trends consists of the development of devices that allow the self-sustained ORR. Indeed, the suppression of air pumping and its associated costs would drastically increase the viability of the technology. In systems with immersed cathodes for ORR, bubbling of external air has been made unnecessary by means of four different approaches. The approach No. 1 addresses the use of the anodic O_2 as the gas source for cathodic H_2O_2 production, thus turning a worthless reaction into a key step. Carbon felt, once coated with carbon black particles mixed with PTFE at a mass ratio of 1:5, yielded more than 10 mM H_2O_2 after 60 min at 5 mA cm^{-2} with no external aeration [322]. In another study, two cathodes (one to promote the ORR and the other one to evolve H_2) were employed in order to evolve a greater amount of O_2 at the single anode. The three electrodes were placed in an upflow flow-through reactor, with the anode at the bottom to allow the transport of all the O_2 toward the cathode of interest [323]. At 5 mA, around 20 mg L^{-1} H_2O_2 were produced. Using an analogous reactor with a single RVC foam as the cathode, Zhou et al. [324] produced a small concentration (i.e., 2.3 mg L^{-1} H_2O_2) at 120 mA from the reduction of O_2 evolved at a DSA mesh. The accumulation of O_2 bubbles may explain the low performance. The same concept but with a different arrangement of two RVC cathodes and two DSA meshes yielded 14.3 mg L^{-1} H_2O_2 after 3 h at 0.8 L min^{-1} and 59.5 mA, reaching a current efficiency of 100% within the first 30 min [325]. Alternatively, the aforementioned microreactors are also appropriate devices to minimize the transport losses of anodic O_2 , given the very short inter-electrode distance. The approach No. 2 is based on the use of electrode rotation to enhance the mass transport of naturally dissolved O_2 . Note that this idea is similar to

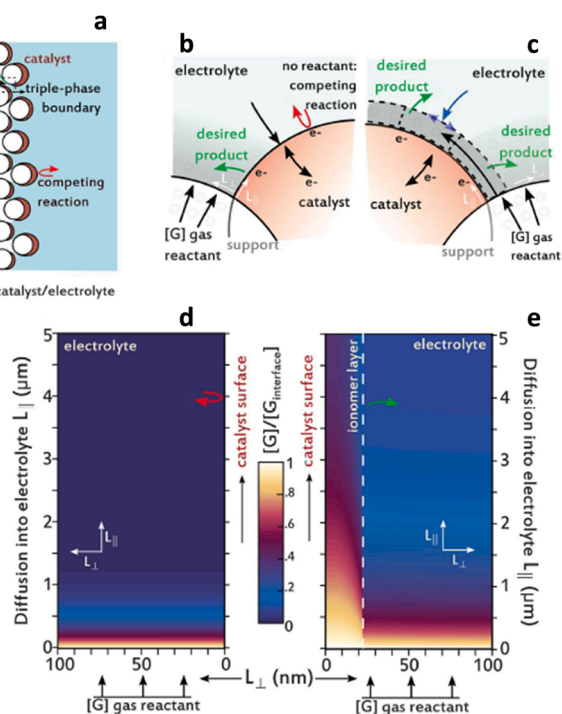


Fig. 23. (a) GDE scheme, showing a hydrophilic side where catalyst particles are in contact with the electrolyte (source of water and ions) in which H_2O_2 is accumulated, and a hydrophobic side that allows the O_2 transport through a PTFE layer. (b) The volume in which gaseous O_2 , catalytic sites and water (and ions) coexist determines the maximum I_{appl} attained from two-electron ORR; a limited reactant (O_2) concentration in some catalyst regions promote parasitic reactions such as the HER. (c) Decoupling of gas and electrolyte transport promotes the extension of the TPB region, so that the parasitic reactions are minimized. (d) Modeled gas reactant availability along the catalyst surface for standard gas transport into a 5 M KOH electrolyte, assuming an in-plane laminar gas diffusivity of $D_{||}/D_{\text{KOH}} = 1000$ for the latter ($D_{||}$ is gas diffusivity parallel to catalyst surface); depending on the gas diffusivity within the gas transport channel, gas availability dramatically increases ($L_{||}$, distance parallel to catalyst surface; L_{\perp} , distance perpendicular to catalyst surface). (e) Idem, for decoupled gas transport (see Fig. 23c).

(b) Adapted with permission from [315]. Copyright 2020 AAAS.

that described above for the RCE cell, but now in the absence of air sparging. In fact, this could be considered an evolution of the first approach, since also the anodic O_2 is transported but more quickly than in the previously explained systems. As an example, two rotating disks made of carbon felt led to the accumulation of $116 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ after 60 min at 5 mA cm^{-2} and 10 rpm, almost thrice the value obtained under static conditions [326]. The approach No. 3 refers to the use of pressurized electrochemical reactors (Fig. 24a), an idea developed by Scialdone. As it is well known, the O_2 solubility increases with pressure and hence, the effect of moderate values (1–11 bar) easily achievable in practice with no requirements of special pipelines was investigated. When pressure was risen from the atmospheric value to 11 bar, the H_2O_2 concentration produced from the ORR at graphite became one order of magnitude greater (i.e., changing from ~ 1 to $\sim 11 \text{ mM H}_2\text{O}_2$ [327]). The final approach, No. 4, seems even more appealing from the point of view of the cost reduction, since it only implies a simple modification in the design of the experimental setup. It is based on the Venturi (i.e., suction) effect that is provoked when the treated solution flows at a high velocity through a constricted area of a tube or pipe. Rodrigo proposed the so-called jet aerator of Fig. 24b, which takes advantage of the abundant entry of air through a hole made in that area, eventually supersaturating the solution and leading to an increased H_2O_2 concentration upon ORR at a carbon felt cathode coated with a carbon black + PTFE mixture [328]. The H_2O_2 concentration reached 960 mg L^{-1} after 180 min at 50 mA cm^{-2} (i.e., current efficiency of 51%). A similar jet-type upflow reactor equipped with a carbon felt coated with a CNTs + PTFE mixture yielded $1418 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ after 120 min at 24 mA cm^{-2} (i.e., current efficiency higher than 90%) [329]. A further innovation of interest resulted from the combination of some of these systems, giving rise to a pressurized jet aerator [330]. As depicted in Fig. 24c, the experimental setup included a microfluidic flow-through reactor.

Regarding the systems equipped with GDEs, the concept of passive air transport or passive aeration has recently allowed the proposal of setups that exclude the air chamber and hence, the air pump. As

commented above, this arises as the extreme case of the hydrophobization strategy, which aims at forming superhydrophobic (i.e., superaerophobic or superwetting) [331] cathodes.

Such materials, once partially exposed to the surrounding atmosphere set in different positions (Figs. 22d and 22e) allow the natural diffusion of air through them, reason that justifies the terms air-breathing [332] and NADE [310,333,334] that some authors employ. In some cases, these cathodes are directly suspended over the liquid surface, with only the hydrophilic CL submerged in the solution. Therefore, they are called floating air cathodes (FACs) [335]. Their scale-up has been recently attempted (i.e., 707 cm^2), yielding a production rate of 196 mg h^{-1} [336]. As explained above, the TPB existence determines the performance of GDEs. The wettability or hydrophobicity/hydrophilicity ratio can be tuned via three phase interface engineering, in particular by modulating the polymer content [300]. The ultimate goal is to reach the underwater Wenzel-Cassie (WC) state, an intermediate structure between the Wenzel (fully wetted surface where O_2 is only available via slow diffusion through the solution) and Cassie-Baxter (fully filled with gas, which almost impedes the H_2O_2 formation) states (Fig. 25).

As long as the WC conditions are stabilized over the electrolysis, the carbon pores remain partially filled with O_2 gas and electrolyte [331, 337], and the ORR is boosted, thereby maximizing the current efficiency. Deep knowledge on the fundamentals of the transition towards the WC wetting state could favor the design of highly efficient cathodes for ORR.

4.2.6. Nanoengineered carbons

In most of the aforementioned studies, raw carbon black particles or 3D carbonaceous materials were employed as cathodes. The addition of nanosized carbons was also attempted, in order to increase the electroactive area and confer new electronic properties that appear at the nanoscale, as tested with CNTs [329] and, more recently, with graphene coatings onto immersed carbon cloth [313] and onto graphite/PTFE

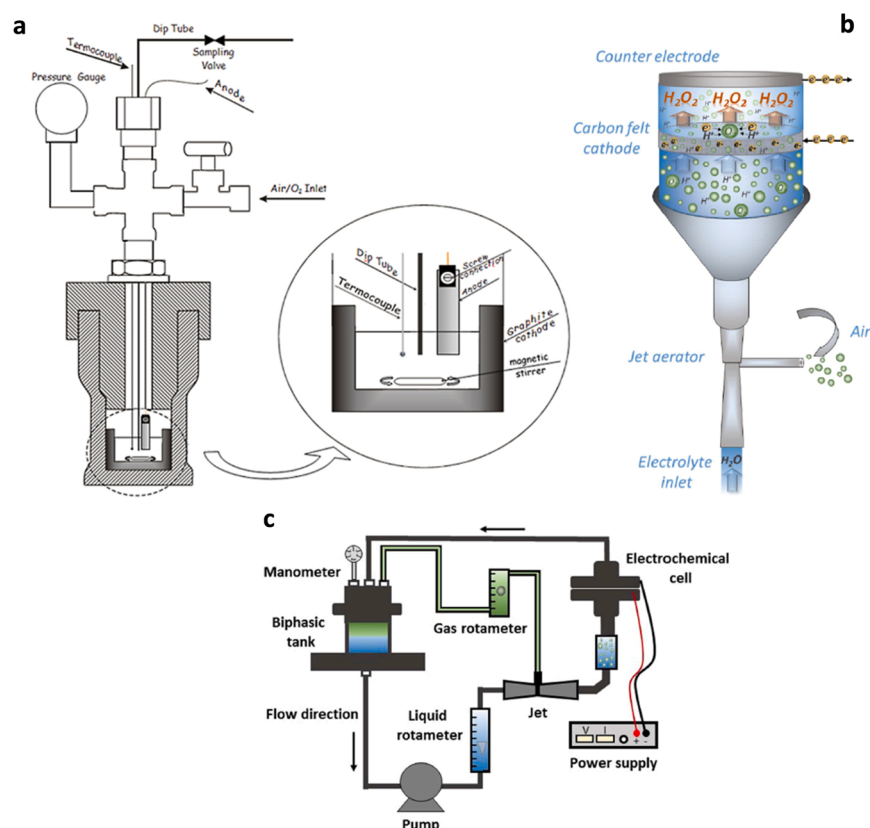


Fig. 24. Sketches of systems employed for H_2O_2 production: (a) Under pressure, alongside a close view to the elements of the electrochemical reactor. (b) With a jet aerator that supersaturates the solution with O_2 , which then flows through a conventional flow-through reactor. (c) With a pressurized jet aerator and a microfluidic flow-through reactor.

(a) Adapted with permission from [327]. Copyright 2015 Elsevier. (b) Adapted with permission from [328]. Copyright 2016 Elsevier. (c) Adapted with permission from [330]. Copyright 2018 Elsevier.

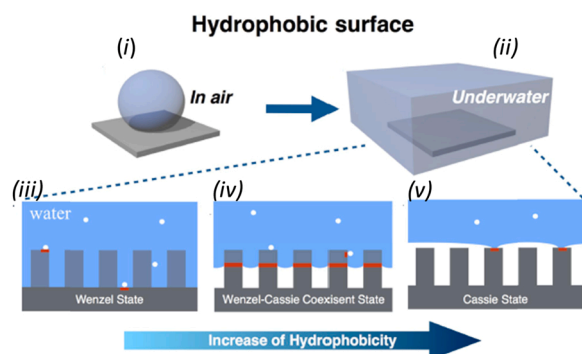


Fig. 25. Sketch of a superhydrophobic surface in air (i) and underwater (ii), with the sample surrounded by air or water, respectively. For the underwater situation, three wetting states are distinguished: Wenzel (iii), Wenzel-Cassie (iv) and Cassie or Cassie-Baxter (v). In each case, the TPB is evidenced in red color. Adapted with permission from [337]. Copyright 2017 Wiley-VCH GmbH.

GDEs [338]. Nonetheless, the modification of the surface characteristics of carbons is known to increase their efficiency for ORR; this may arise from their greater selectivity, as a result of the shifting of the reduction potential to more positive values (i.e., decrease of the overpotential for reaction (41)), and/or activity [261]. As a premise, the active materials for ORR usually exhibit a trade-off between selectivity and activity; it is thus necessary to reach an optimum compromise: select or design a material that yields the highest current efficiency (related to the H_2O_2 selectivity) once determined which is the maximum time that can be devoted to the water treatment. For this, a rational catalyst design has been carried out by many researchers. The latest advances related to metal-free carbon materials respond to two main objectives: (i) Finding new routes to synthesize more eco-friendly carbons than those manufactured from hydrocarbon combustion, in agreement with modern policies on sustainability, circular economy and green chemistry, and (ii) enriching the surface chemistry of carbons to enhance their catalytic properties. The most remarkable strategy to achieve the first objective has been based on the synthesis of biomass-derived carbons. This is not really a new topic because the idea dates back at least a decade, although it can be certainly considered innovative within the context of H_2O_2 production for advanced water treatment [339]. In the particular case of GDEs, this is definitely a novel subject, as explained in some recent works and references therein [340,341]. These authors prepared carbons from glucose, chitosan and agarose, demonstrating that they can be competitive as compared to commercial carbons. For example, agarose-derived GDEs with enhanced textural properties (i.e., area, pore distribution and graphitization degree) and an optimized combination of micropores and mesopores volume, attained a Faradaic efficiency of $\sim 95\%$ at 30 min [342]. The obtention of mesoporous carbons is a trend nowadays, as they favor the mass transport, which limits the residence time of H_2O_2 near the cathode surface and minimizes its destruction. However, this should be wisely combined with microporosity, as it offers a higher internal surface area (i.e., more active sites) and stronger binding of gases like O_2 . The second objective can be accomplished through pre-treatments, such as chemical or electrochemical activation/modification. The suspension of carbons in sufficiently acid or alkaline media [343], as well as solvothermal or plasma treatments, tend to induce the doping of carbon with functional groups and, sometimes, defects, which are known to be active regions with increased reactivity. Oxygen, the most typical heteroatom resulting from these pre-treatments, has an extraordinary positive effect on the ORR efficiency [344], with proven enhancement of activity and selectivity that follows an almost linear correlation with O content [345]. Carbon atoms in adjacent positions to oxygen-containing functionalities like $-\text{COOH}$ or $\text{C}-\text{O}-\text{C}$ behave as especially active sites [345,346]. The effect of other heteroatoms such as nitrogen, sulfur, boron and phosphorus has also

been investigated. Particular emphasis has been put in N-doping through the appearance of different N-functionalities (pyridinic, imine, amine and pyrrolic N). These groups, particularly the pyrrolic N [341], are favorable for H_2O_2 production because they give rise to new active sites, facilitate the O_2 chemisorption and increase the hydrophilicity of the carbon surface [261]. Co-doping with N-doping and O-doping [347] or S-doping [348,349] has been recently reported, showing for example that the catalytic activity follows a linear dependence with the N content [348].

Apart from being an excellent material to promote reaction (41), carbon is an optimum substrate to support metal electrocatalysts designed ad hoc to increase the performance. Progress in carbon-supported materials as cathodes for H_2O_2 synthesis is based on doping strategies that lead to the decoration of the carbon surface with different structures, from particles to single atoms (i.e., metal atoms atomically dispersed on 2D surfaces). Worth commenting, although the main purpose of the surface modifier should be the enhancement of the H_2O_2 production (in terms of selectivity and/or activity), a dual role has been conferred in some cases, as it can simultaneously serve as catalyst for Fenton's reaction (see comments on heterogeneous electro-Fenton (EF) in Section 4.2.3). Regarding the use of NPs, as a first type of modification, guidance for rational electrocatalyst design has been provided in some thematic reviews, which highlight the role of electronic phenomena induced by the particles, as well as the influence of their geometry, structure and dimensions [350]. The ORR to H_2O_2 from reaction (41) requires the preservation of the O-O bond and sufficient H^+ transport toward the cathode surface. Therefore, the adsorption energy of the OOH^* intermediate species on the carbon-NP composite plays a fundamental role in the H_2O_2 production rate. Au-Pd NPs on glassy carbon [351], as well as Pt-Hg and bimetallic Pt-Pd NPs immobilized on RVC GDE showed a high performance for H_2O_2 synthesis [261], but the most recent trends in water treatment aim at promoting the use of noble-metal-free catalysts with lower cost [352]. The group of Lanza is very active in the manufacture of GDEs modified with a range of NPs. For example, they performed the electrochemical characterization of a Ta_2O_5 /carbon black catalyst, whose RRDE efficiency ($\sim 83\%$) clearly overcame that of the pristine carbon ($\sim 65\%$). The superiority of the modified carbon was confirmed upon bulk electrolysis with the corresponding GDEs, enhancing the H_2O_2 concentration from 19.1 to 27.9 mg L^{-1} [353]. Carbonaceous carbons decorated with Co-based NPs have also been proven highly effective to produce H_2O_2 . Several Co chalcogenides have been studied so far and, in particular, CoS_2 with pyrite structure revealed an excellent behavior during tests performed at small scale and in a pilot plant of 2.5 L. Upon partial substitution of S by P atoms, which conferred a much greater stability of the catalysts before use, a high H_2O_2 productivity (12 mM) and current efficiency (higher than 50% for 6 h) was found at 25 mA cm^{-2} using a GDE (20 cm^2) modified with CoSP/MWCNTs [354]. Fe-loaded carbons have also been studied, employing a variety of iron sources like zero-valent iron, iron oxides and sulfides or bimetallic NPs containing iron. Most of these studies address the use of the cathode not only for H_2O_2 production but for simultaneous heterogeneous Fenton's reaction. As an example, graphene-supported Fe_3O_4 yielded a greater current density as compared to that supported on Printex carbon, showing a high selectivity and excellent durability [355].

Redox mediators like Sudan Red 7B azo dye have also been tested as possible modifiers [293] but, overall, this seems a less appealing approach for practical application, as the organic molecule is expected to suffer from gradual degradation as the electrolysis proceeds. The other important procedure to modify the carbon surface, still less explored than that based on NPs but progressively becoming a hot topic in the context of electrocatalysis, regards the doping with atoms. The preparation of high-performance catalysts at the atomic scale, such as SACs, single atom alloys (SAAs) and single cluster catalysts (SCCs) has become the forefront of catalysis investigation due to the reduced costs and the maximized atom utilization efficiency arising from the smaller

size and the enhanced activity. At this point, the reader is invited to revise some recent critical reviews that serve as a guide for the rational design of SAAs [356] and SACs for environmental applications [357]. In a nice example of atomic-level tuning, a Co-N₄ moiety incorporated in N-doped graphene (NG) was evaluated as a new catalyst for H₂O₂ electrosynthesis [358]. Co₁-NG(O), which accounts for a complex configuration in which the Co metal center is close to an adsorbed O atom, exhibited an unprecedented electrocatalytic reactivity for two-electron ORR, much greater than that shown by expensive noble metal-based catalysts. In addition, there was no significant activity loss for at least 110 h. The superiority of this atomic configuration as compared to others can be inferred from Fig. 26a. The binding energy of the key intermediate OOH* (Fig. 26b) was used as descriptor to assess the activities and selectivities. In this material, individual Co atoms were uniformly embedded in the graphene matrix when a concentration of 1.4 wt% Co was employed. However, as the Co amount was increased, Co atoms agglomerated and nanoclusters were formed, as can be observed for 2.16 wt% Co in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Figs. 286c and 26d. This agglomeration was detrimental, resulting in a lower electrochemical H₂O₂ production (i.e., lower ring current and H₂O₂ selectivity). SACs from other metals such as Pt, Ni and Co-Mo [359] have been successfully tested for H₂O₂ electrosynthesis. Among them, particularly relevant is the study of a carbon-supported Ni SAC with current efficiency of 96% that was further used to prepare a GDE and produce H₂O₂ in a flow cell for 8 h [360].

As a final remark, carbons with a very large surface area and abundant micro/meso/macropores rich in catalytic sites, which are suitable for an enhanced H₂O₂ production, have been lately synthesized from highly porous precursors like zeolitic imidazolate frameworks (ZIFs) and metal-organic frameworks (MOFs). ZIFs and MOFs can be prepared via simple solvothermal procedures before undergoing a pyrolysis step. Depending on the reagents employed and the conditions of the synthesis and the thermal treatment, a wide variety of carbons doped with metals and heteroatoms can be obtained [361], which offers a very rich chemistry. Note that SACs and SCCs can also be derived upon an accurate manufacture of such carbons.

4.2.7. •OH-based AOPs: H₂O₂ photolysis and H₂O₂ reduction

The previous paragraphs have shown the increasing interest in finding better cathode materials and electrochemical reactors to produce H₂O₂ on site. However, in environmental electrochemistry this is just a first step because H₂O₂ is actually a mild oxidant that is quite ineffective against the majority of organic contaminants. In fact, only at sufficiently high concentration it can find an application in water disinfection and color removal. In our past review [1], the EO-H₂O₂ process was described as a smart coupling strategy that increases the overall oxidation power of the system and maximizes the current efficiency. In EO-H₂O₂, a typical anode with great ability to evolve O₂ is replaced by materials that foster the production of M(•OH) and/or Cl₂ (see Sections 2 and 3), which enhances the decontamination and disinfection performance. Since then, two new approaches have been attempted aiming to further increase the performance of the water treatment. They promote the activation of the generated H₂O₂, leading to the formation of the powerful oxidant •OH as a free (i.e., homogeneous) radical species in the bulk solution.

The first one is based on the H₂O₂ activation by UVC light, which causes the homolysis yielding 2 mol of •OH per mol of H₂O₂. The so-called H₂O₂ photolysis process is widely extended even at industrial scale, as for example through the Wedeco MiPRO device commercialized by Xylem Water Solutions. As an alternative, the H₂O₂ can be electro-synthesized in situ in an electrochemical reactor coupled with a UVC photoreactor. Barazesh et al. [362] employed a divided cell equipped with a GDE (carbon paper coated with graphite + PTFE, projected surface area of 64 cm²). The solution to be treated flowed as catholyte to be enriched with H₂O₂ (1–2 mM, with Faradaic efficiency around 88%) and, once irradiated by the low-pressure UV lamps, it was recirculated as the anolyte to remove the residual H₂O₂. Note that this latter step was also beneficial for ensuring a deeper degradation of the trace contaminants upon the action of both, direct oxidation and mediated oxidation by the oxidants generated at a DSA plate. The system, with capacity to treat up to 120 L water d⁻¹, was validated with simulated water and urban wastewater, and the cathode performance was stable during long-term experiments.

The second strategy relies on the electrochemical activation of H₂O₂.

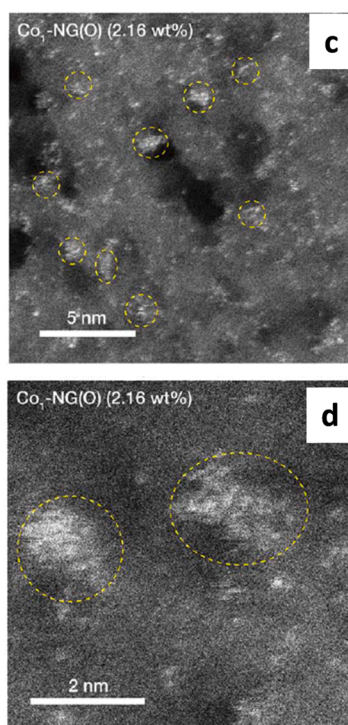
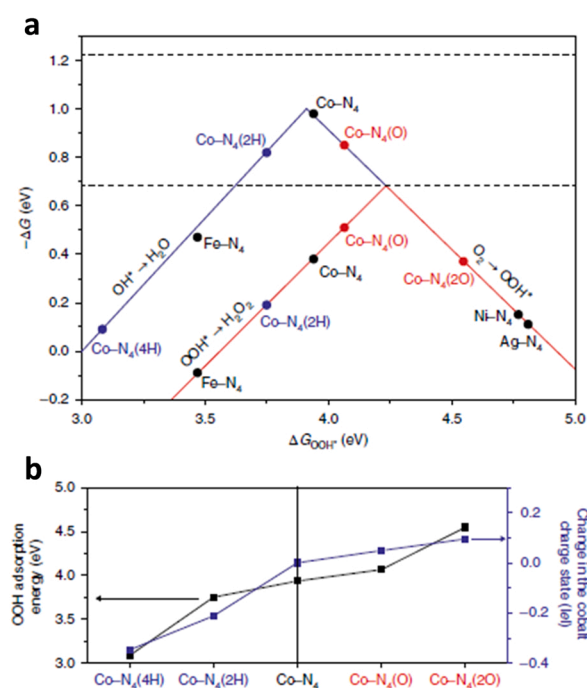


Fig. 26. (a) Theoretical catalytic activity volcanoes for the four-electron (blue line) and two-electron (red line) ORR. Black data points account for M-N₄/graphenes used to construct the activity volcanoes. Blue and red data points represent Co-N₄/graphenes with 4 H^{*}/2 H^{*} and O^{*}/2 O^{*} adsorbed near the Co atom, respectively. (b) Calculated OOH* adsorption energies and relative charge states of the Co metal centre in Co-N₄/graphene with and without neighboring adsorbed H^{*} and O^{*}. (c, d) HAADF-STEM images of Co₁-NG(O) with 2.16 wt% Co, at two magnifications. Adapted with permission from [358]. Copyright 2020 Nature Publ. Group.

Some authors defend the formation of $\bullet\text{OH}$ from either the cathodic monoelectronic reduction of H_2O_2 (reaction (42)), as detected by ESR spectroscopy. Similarly, the decomposition of H_2O_2 on the surface of granular activated carbon (GAC) acting as a particle electrode is suggested to proceed via $\bullet\text{OH}$ as intermediate. Both examples represent metal-free H_2O_2 -based AOPs, a potentially interesting alternative to Fenton-based processes that are highly sensitive to pH (see subsection 4.2.3). Note also that the concomitant formation of superoxide radical via reaction (43) has been proposed in some studies [363].

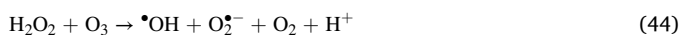


The first study of this kind reported the occurrence of reactions (42) and (43) at the surface of a GDE, made with carbon black + PTFE, modified with a reduced graphene oxide layer and fed with naturally diffusing air [363]. The high effectiveness of the generated species was deduced from the complete degradation of bisphenol A at neutral pH. The authors attributed the phenomenon to the contribution of the O-containing functionalities and the defects as active sites present in the graphenic layer. In a similar manner, N-doped graphene coated on carbon felt showed a high ability to degrade phenol upon the action of $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$, as detected by ESR [364,365]. N-doping disrupts the sp^2 hybridization, thus creating new active sites for H_2O_2 activation, although attention must be paid to poisoning of such sites with organic matter, especially in actual wastewater. O-doped CNTs [366] and porous carbon monoliths [367] have been recently employed to carry out the same process.

Although the activation of H_2O_2 to $\bullet\text{OH}$ has been proposed since several years ago for activated carbons [363], the excellent results reported in the works cited above require a surprisingly high production of $\bullet\text{OH}$ from reduction (42). This seems quite unexpected as compared to those obtained in other H_2O_2 -based processes and hence, further investigation is needed.

4.2.8. $\bullet\text{OH}$ -based AOPs: Coupling via electro-peroxone process

The combination of H_2O_2 and O_3 , so-called peroxone, is highly effective for the degradation of organic pollutants due to the production of $\bullet\text{OH}$ via reaction (44) [368], sometimes expressed according to reaction (45) [369]. Based on such good behavior, the electro-peroxone (i. e., E-peroxone) process was further developed, with the main feature of producing the H_2O_2 in situ according to the multiple approaches explained in subsection 4.2. E-peroxone is more cost-effective and safer than its non-electrochemical counterpart, and it does not require any catalyst, unlike the Fenton-based processes.



The first works combined the electrogenerated H_2O_2 with O_3 produced by means of ozone contactors fed with O_2 . This is an interesting setup from a practical standpoint, since the available ozonation equipment can be easily adapted and upgraded to give rise to the E-peroxone process. One of the drawbacks inherent to the electrochemical system is the possible destruction of O_3 via cathodic reduction reactions (46) or (47) [370]. In fact, the O_3 reduction is thermodynamically favored over the ORR to H_2O_2 , which could be inhibited at sufficiently high O_3 concentrations. Luckily, small O_3 amounts are dissolved in practice and hence, its reduction is limited by mass transport. Despite this, it is advisable to select cathode materials that minimize these two destruction reactions.



The first publication on E-peroxone reported the degradation of

Methylene Blue dye- H_2O_2 was produced at a C/PTFE cathode from O_2 sparged into the solution, whereas O_3 was produced at an ozonator [368]. Note that the sparged O_2 is actually that unreacted during the O_3 production, which increases the efficiency of the typical ozonation process. The carbonaceous cathode can serve as a platform for multiple events, offering the possibility to combine an adsorption process that enhances the degradation performance thanks to the pre-concentration of the organic molecules prior to their treatment by E-peroxone. This was shown by Huang et al. [371] for the complete degradation of diclofenac, using a cathode consisting in a Ni mesh coated with a MWCNTs + PTFE mixture. More recently, the E-peroxone process has been tested in a flow-through electrochemical reactor equipped with a DSA mesh and a cathode made of graphite felt coated with a carbon black + PTFE mixture [372].

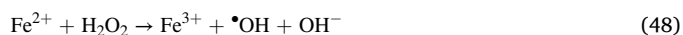
The use of GDEs instead of immersed cathodes is a viable alternative for ensuring that a sufficiently high concentration of H_2O_2 is attained, which could be at risk by the competitive O_3 reduction. A comparison between both types of cathodes revealed that carbons are suitable materials for E-peroxone, but GDEs are superior due to the higher H_2O_2 production rate [373]. In another work, a 3D-like GDE, made of graphite felt put in contact with a carbon cloth, was implemented in a filter-press cell equipped with an air-chamber to feed compressed air ($P = 3$ psi) to the cathode. The complete color removal and 60% mineralization were achieved [374].

Considering that ozonators can only transform a small percentage of O_2 into O_3 , a fully coupled electrochemical system has been recently devised, allowing the simultaneous electrosynthesis of H_2O_2 and O_3 at the cathode and the anode, respectively. In this way, the O_3 produced electrochemically is already dissolved into the solution, not requiring the dissolution step, which becomes beneficial to accelerate its reaction with H_2O_2 . Yang et al. [369] addressed this coupling strategy using a cell equipped with a GDE to produce H_2O_2 and a $\text{Ti}_{\text{mesh}}|\text{PbO}_2$ anode to evolve O_3 , achieving the complete degradation of carbamazepine.

Since many parameters such as the applied current, the O_3 dose or the reactivity with the components of the treated solution can affect the reaction mechanisms and the degradation kinetics, new upgrading of the foundational process is needed. For example, the photoelectro-peroxone process has been recently developed, taking advantage of the O_3 and H_2O_2 photolysis caused by UV light.

4.2.9. $\bullet\text{OH}$ -based AOPs: coupling via electro-Fenton and related processes

The third family of processes shares the activation of H_2O_2 by a metal catalyst as common feature, being the mixture of both species known as Fenton's reagent. A large quantity of $\bullet\text{OH}$ is generated in the solution bulk upon the occurrence of the Fenton's reaction (48), as widely demonstrated since the first mechanistic studies by Haber and Weiss. However, some controversies have appeared over time, giving rise to a less classical interpretation that suggests the formation of hypervalent iron complexes as main oxidizing species [48]. Moreover, the cogeneration of $\text{O}_2^{\bullet-}$, HO_2^{\bullet} and singlet oxygen as reactive oxygen species (ROS) has also been suggested. This part of the review presents a brief description of the fundamentals, as well as of the innovations on cathodes, catalysts and reactors developed in recent years to carry out the EF and other related processes. More information about recent advances has been recently discussed by experts in the field [293,375].

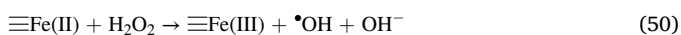


4.2.9.1. A wide variety of processes. Although the first application of the EF process to water treatment dates back around fifty years, the series of works performed from the mid-nineties at the research groups led by Brillas and Oturan actually inspired the newcomers [48]. Consequently, this has become a very hot topic in the last decade, as deduced from the current extraordinary world impact of the investigation area. The in situ

cathodic H_2O_2 electrogeneration, explained with detail in subsection 4.2, distinguishes the EF and related processes from their non-electrochemical counterparts. Depending on the cathode characteristics and the operation mode, the regeneration of the Fe^{2+} catalyst via reaction (49) can also emerge as a distinct feature that allows maintaining the catalytic $\bullet\text{OH}$ production. In general, the system is operated under electrolytic conditions (i.e., constant I_{appl} or E_{cath}) that ensure the production of sufficiently high H_2O_2 concentration. However, some authors have run the experiments under an optimum E_{cath} for promoting reaction (49) over reaction (41) in order to minimize the iron co-precipitation that may be observed on the cathode surface at an excessively large cathodic overpotential [376].



The conventional homogeneous EF and related processes perform optimally at pH around 2.8 [293]. Nonetheless, the so-called heterogeneous EF has appeared as an alternative when working at more alkaline pH (see below), relying on the occurrence of the heterogeneous Fenton's reaction (50) on the surface of Fe-rich or Fe-loaded solid compounds.



where \equiv represents the solid state.

Note that, from the point of view presented in Section 2, the EF process can be considered a mere coupling between cathodic H_2O_2 electrosynthesis in the presence of a metal catalyst and anodic oxidation. Other types of coupling have derived in a family of technologies that are appealing not only in the water treatment sector but also beyond it [377]. For example, when the electrochemical reactor is not equipped with suitable cathodes for the efficient promotion of reaction (49), the Fe^{3+} ions formed from Fenton's reaction (48) are readily complexed by certain organic intermediates that act as chelators. This results in the accumulation of metal-organic complexes that may be highly resistant to the attack of any ROS, as in the case of Fe(III)-carboxylate complexes. The irradiation of the treated solutions with UVA photons from UV lamps or natural sunlight, which gives rise to the photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF) processes, has a dual positive effect: (i) the photodecomposition of the complexes, which frees Fe (II) and enhances the mineralization as the organic ligand (L) is released, according to reaction (51); and (ii) the catalyst photoregeneration via photo-Fenton reactions (52), which can occur both homogeneously or heterogeneously. Note that the most stable Fe(III) species at the working pH can be an iron-hydroxo complex and hence, reaction (52) would also contribute to the generation of an additional amount of $\bullet\text{OH}$ [48].



The superiority of SPEF over PEF has been usually attributed to the greater power of the sunrays, since the most common UV lamps have between 4 and 300 W. Additionally, the wider spectral range allows increasing the extent of the photoreduction reactions (51) and (52). In particular, the UVC photons in natural sunlight cause the photolysis of the aromatic molecules and the partial homolytic H_2O_2 photodecomposition. The positive contribution of UVC photons in PEF process has been recently described [378].

Another possible coupling arises when the anode of the typical EF cell is replaced by a soluble one, like Fe or mild steel. This gives rise to the peroxi-coagulation process, in which the organic pollutants are partly mineralized, owing to the occurrence of Fenton's reaction in the presence of in situ generated iron ions, and partly coagulated due to the massive production of hydroxide and iron ions (i.e., Fe(OH)_3). This process was first developed by Brillas using a GDE as cathode [48], but lately some authors have performed it with modified carbon felt as a cheaper material [379], or with a NADE to avoid the use of the air compressor [380]. The energy consumption can be lower as compared to

EF or electrocoagulation processes, although the sludge post-treatment must be considered in the economic balance.

As a last remark, note that, if an Fe(III) species or metal species different from iron are employed as catalyst, the name of all the abovementioned processes slightly changes to their "like" form (e.g., EF-like). As will be shown hereby, the latest investigations are prioritizing the improvement and optimization of different elements of the system: cathode, catalyst and reactor. The details about the anode, which is also an essential element because it contributes to the production of oxidants that can act simultaneously with the aforementioned ROS, have been discussed in Sections 2 and 3.

4.2.9.2. Newly-developed cathodes. Some of the studies about cathode improvement described in subsection 4.2 were not only focused on their ability to electrogenerate H_2O_2 , but also on their application in EF and related processes. Therefore, those references serve as a good prelude to this part. As mentioned in that previous subsection, significant progress has been made in recent years thanks to the development of new cathodes, most of them based on carbon due to its excellent properties. Although GDEs, manufactured with carbon paper and carbon cloth as support, and 3D porous carbon felt are the two most widespread types of cathodes for EF and related processes, some authors have addressed their modification [261], as summarized in Table 1. For example, employing a graphene ink-coated carbon cloth, with Nafion as binder and dispersant, the mineralization of a 1.4 mM phenol was upgraded by 15% as compared with the uncoated cloth [313]. The positive influence of the increased surface area on the EF performance has also been observed using CNTs.

The decoration of the carbon surface with nonprecious metal-based NPs is another task with great dissemination in many research fields due to its simple scale-up. A nice example is related to the manufacture of CoSP-decorated MWCNTs, which served to increase the electroactive surface of GDEs prepared with either carbon cloth [381] or carbon paper [354] as substrate. Pyrite-type CoS_2 -based particles have been proven efficient for H_2 evolution from water and highly selective ORR to H_2O_2 [354]. However, they suffer from lack of stability, which can be greatly solved upon partial substitution of S atoms by P because the surface oxidation is minimized or prevented. In these studies, solutions of 2.5 L of the preservative bronopol (0.28 mM) and the herbicide bentazon (20 mg L^{-1}) were treated in recirculation batch mode. SPEF with a BDD anode led to the complete removal of the former pollutant after 210 min at 40 mA cm^{-2} , with 94% mineralization at 360 min [381], whereas PEF with BDD yielded the total removal of the herbicide after 20 min at 25 mA cm^{-2} , with 77% mineralization at 240 min [354].

Carbon doping is another effective strategy, since the incorporation of heteroatoms may enhance the physicochemical properties, the specific surface area and the pore volume of the material [382]. In order to synthesize heteroatom-doped carbon materials (HDCMs) for application in the electrochemical Fenton-based water treatment, single-atom

Table 1
Latest studies describing new cathodes and heterogeneous catalysts used in EF and related processes.

Newly-developed carbonaceous cathodes	Ref. [313]
Carbon-coated substrate	
Decoration with metal-based NPs	[354,381]
Doping with heteroatoms	[346,349,383,384]
Biomass-derived carbons	[341,342,385–390]
Heterogeneous catalysts	Ref.
<i>Supported</i>	
Iron oxides or sulfides	[403,405,406]
LDHs	[404]
<i>Suspended</i>	
Iron oxides or sulfides	[375,391,408–411]
Fe-based MOFs	[412–414]

doping and multiple heteroatom doping have been attempted. Oxygen is one of the most common dopants because it can be easily introduced following simple oxidation routes. As an example, O-doped carbon felt was prepared via hydrothermal activation in HNO_3 . The resulting material contained diverse surface O-functionalities like C-OH, H-O-H, C=O and O=C-OH, more notably the latter two, which preeminently adsorb the O_2 molecule in end-on mode (i.e., Pauling mode, involving one O atom in a perpendicular position to the active sites) that favors the two-electron ORR. The highest activity in the EF treatment of the antibiotic levofloxacin was observed using a cathode with an O/C ratio of 0.162, yielding a faster degradation kinetics than EF with other modified carbon felts reported in the literature [383]. Air calcination is also able to induce the formation of O-containing functional groups such as O=C-OH and C-O-C. A modified carbon black was employed to prepare a FAC, which allowed attaining a 91% Rhodamine B (10 mg L^{-1}) degradation in 2 min with 76% mineralization after 32 min upon EF treatment [346]. Nitrogen is the other key heteroatom for promoting the ORR to H_2O_2 and hence, to enhance the EF performance. In the presence of N, a delocalized conjugated system is created between the carbonaceous backbone (sp^2) and the lone electron pairs of N atoms. This positive contribution was verified by several authors, for example doping carbon-felt cathodes using hydrazine as N source [384]. The EF treatment of 500 mL of solutions of levofloxacin at pH 3.0 was much more efficient than that carried out with undoped carbon felt. Similarly, co-doping with S atoms has been proven positive, since the N atoms favor the end-on adsorption of O_2 and the S atoms modulate the binding of the OOH^* intermediate. The significant enhancement of H_2O_2 production using an N,S-doped GDE in EF led to the complete removal of several sulfonamides in 60 min [349].

The latest trend among carbonaceous cathodes used in EF and related processes is referred to the use of cheap biomass as the source of carbon, yielding the so-called biochar. By selecting biomasses that naturally contain heteroatoms like N or S, the pyrolysis step incorporates these atoms as well as O in the resulting carbon, which is expected to enhance the degradation performance. Carbons derived from different biomasses like water hyacinth [385] giant reed [386], straw [387], bamboo [388], sucrose [389] or cellulose [390] have been either supported on substrates such as Ti mesh, Ni foam, carbon felt and carbon paper or kept as self-standing carbons to produce H_2O_2 from dissolved O_2 . These cathodes were effective to degrade organic pollutants like dimethyl phthalate, sulfamerazine, Rhodamine B, clothianidin, sulfanilamide and various phenolic compounds by homogeneous and heterogeneous EF processes. On the other hand, the number of works reporting the preparation of GDEs made with biomass-derived carbons and their testing in EF and related processes is much scarcer. This is thus a quite unexplored field with a great deal of possibilities in the future. In the two first studies on this topic, chitosan [341] and agarose [342] were selected as abundant carbon sources. The former is an N-containing biopolymer, whereas the latter is a fraction of a polysaccharides mixture called agar, obtained from marine red algae cells. Depending on the synthesis conditions, a range of surface areas and mesoporosity/microporosity ratios could be achieved, which had a direct impact on the performance of the GDEs and hence, on the EF and PEF treatments of acetabulol. Solutions of 150 mL of this pharmaceutical at pH 3.0, with FeSO_4 as catalyst source, required 16 min to completely remove it at 30 mA cm^{-2} via PEF using the chitosan-derived N-doped carbon, whereas PEF with a GDE prepared with undoped carbon needed 20 min [341]. Steam treatment had great influence on the textural properties of the agarose-derived carbons, reaching the total drug removal in urban wastewater after 60 min at an I_{appl} as low as 10 mA cm^{-2} [342]. Note that some of these green carbons exhibit a large surface area, especially if adequate activation treatments are applied. Aiming to obtain as much surface area as possible without requiring a specific activation, porous structures like ZIFs and MOFs have been recently taken as platforms to synthesize carbons with very high porosity. Porous carbon materials are beneficial because of the fast mass

transport and greater accessibility to active sites. In two recent examples, carbon fibers were coated with carbon obtained from ZIF-8 pyrolysis [391], whereas carbon paper was coated with carbon obtained from an N-containing MOF (i.e., Zn pyridine-2,6-dicarboxylate) [392]. The former was used to degrade tetracycline in 20 min, with 83% mineralization as maximum, whereas the latter was employed to degrade some antibiotics (97%–98% in 10 min), with 71%–92% mineralization in 60 min

4.2.9.3. Catalyst selection and design. The EF and related processes were initially envisaged as powerful technologies for the degradation of organic pollutants in acidic medium, and their use was planned to be circumscribed to pH values up to 3.0, with optimum pH for Fenton's reaction (48) around 2.8. Soluble iron salts, in particular FeSO_4 , are usually chosen as catalyst source to reach the highest efficiency of conventional homogeneous EF, PEF and SPEF processes run at acid pH. If a cathode with large ability for Fe^{3+} electroreduction is employed, a cheaper salt like $\text{Fe}_2(\text{SO}_4)_3$ can also serve as an indirect source of Fe^{2+} [375]. Some authors have proposed a sequential two-step treatment, in which an electrocoagulation cell was first employed to coagulate a substantial amount of organic load and dose a small concentration of iron ions, whereupon the solution was treated by Fenton-based EAOPs in a cell equipped with a cathode able to produce H_2O_2 . The effectiveness of this coupling was demonstrated for degrading organic pollutants like bronopol [393], as well as for disinfecting urban wastewater [394]. Note that this combined system presents advantages over the one-pot peroxi-coagulation treatment, which suffers from the aggressive action of the iron hydroxides formed [379,380].

In some industrial premises, the mixing of streams with different pH is routine. Hence, it is sometimes possible to acidify an effluent before its EF treatment, at zero cost. Nonetheless, in recent years, there has been growing interest in expanding the operation pH range in order to widen the applicability to the treatment of more alkaline industrial effluents or even natural water [293]. In such cases, conventional soluble iron is not effective, owing to the iron hydroxide precipitation. Historically, this has been a critical shortcoming of all conventional Fenton processes. The pH regulation and control would be an alternative, but it may be expensive and time consuming, especially when dealing with large water volumes. Therefore, either new forms of soluble iron or Fe-rich and Fe-loaded solids have been brought into action by following selection or design strategies. A priori, the first approach is more interesting, since it allows maintaining the fast degradation kinetics that results from the quick volume diffusion of the two Fenton's reactants. Iron (i.e., Fe(III)) can be kept soluble at pH greater than 3.0 by means of chelators, giving rise to organometallic catalysts. The most classical ones include citrate, oxalate and tungstate as ligands of the metal center, being still employed at present due to their relatively low price [395]. Recently, aminopolycarboxylic acids like ethylenediaminetetraacetic (EDTA), nitrilotriacetic (NTA), and ethylenediamine- N,N' -disuccinic (EDDS) have been developed as novel chelators in the context of non-electrochemical Fenton processes, thereby being introduced in their electrochemical counterparts, which has widened the applicability of homogeneous catalytic water treatment at mild pH [396]. Among them, EDDS seems a more adequate choice because of its higher biodegradability. Mailhot and co-workers were pioneers in the introduction of EDDS in Fenton-like and photo-Fenton-like processes. Very recently, the performance of the Fe(III)–EDDS complex to run the EF-like process has also been evaluated, comparing the results obtained with a carbon-felt cathode and a GDE [397]. The former cathode outperformed the GDE, despite the much lower H_2O_2 electrogeneration, because of the greater and continuous regeneration of Fe(II). This ion, either uncomplexed or complexed with EDDS, promoted the formation of $\cdot\text{OH}$ from classical Fenton's reaction (48) and an analogous alternative Fenton-like reaction. Its contribution to initial TOC, the scavenging effect on $\cdot\text{OH}$ and its gradual destruction are the main concerns when using EDDS, as also

occurs with the other organic ligands. Worth mentioning, the EF-like process is superior to the respective Fenton-like treatment because of the positive effect of I_{appl} . A similar effect in systems with a GDE as the cathode can be achieved upon photoirradiation (i.e., under PEF-like conditions), as has been proven for the degradation of the antidepressant fluoxetine in urban wastewater at pH 7.2 [398]. The Fe(III)–EDDS complex is more photoactive (i.e., higher quantum yield) than the Fe(III)–hydroxo complexes, as well as those formed with conventional chelators (reactions (51) and (52)), leading to a greater Fe^{2+} regeneration from photo-Fenton-like reaction (53). This has been attributed to the enhanced ligand-to-metal charge transfer (LMCT), showing higher molar absorption coefficients in the near-UV, which adds to its ability to absorb in the visible region.



Looking for a higher sustainability of this process, the feasibility of the SPEF treatment with the Fe(III)–EDDS complex was verified by degrading the pesticide triclopyr in a pre-pilot plant of 2.5 L equipped with a filter-pressed cell that contained a GDE [399].

NTA has been suggested as an alternative to EDDS, for example for the EF-like treatment of phenol solutions using a flow-through reactor [400]. However, EDDS is a more suitable ligand than citrate, oxalate and the two most widely used polydentate carboxylic acids (NTA and EDTA) due to its larger biodegradability [397]. Polyphosphate electrolytes such as tripolyphosphate, tripolyphosphate and pyrophosphate have also been employed recently in EF-like systems [401]. Finally, note that organic fertilizers are emerging as eco-friendly chelating agents in recent times.

The other option to operate at circumneutral or alkaline pH is based on the use of solid iron forms. Theoretically, the heterogeneous catalysts allow operating within a large pH range as in the case of homogeneous catalysts, although avoiding the need of final neutralization for catalyst separation and the consequent sludge management [402]. The Fe(III) to Fe(II) recycling becomes the rate-determining step, being too slow in many of the materials selected in the literature, which retards the degradation. Furthermore, if a high stability is not ensured, a typical drawback of such solid catalysts is the metal leaching and the gradual dissolution upon use and reuse, which limits their lifetime. Dissolution is especially relevant under acidic conditions and hence, the application of this type of catalyst should be limited to higher pH values. It is then crucial to evaluate the catalyst stability in prolonged electrolytic trials, as well as upon consecutive degradation cycles. In general, a clear superiority of hetero-PEF over hetero-EF has been reported, ending in a faster water decontamination. Although many authors do not assess the mechanisms involved, homogeneous and heterogeneous processes may actually take place, as it is certainly difficult to impede some metal leaching. As shown in Table 1, there are two possible strategies to carry out the heterogeneous catalysis [375,402]: (i) the use of supported Fe-based particles, either on substrates like carbonaceous cathodes or on fixed elements like membranes and resins, and (ii) the addition of Fe-rich or Fe-loaded solid catalysts to the solution, thus remaining in suspended form. A large plethora of materials have been tested as catalysts for these two purposes: Fe-based particles and NPs like iron oxides, iron sulfides and zerovalent iron (ZVI); Fe-loaded carbons, zeolites, silica, resins, biosorbents, hydrogels; natural Fe-rich minerals (e.g., goethite, magnetite), soils and clays (e.g., vermiculite) and waste materials like flyash [375]. The latter group is in good agreement with new policies on waste minimization and circular economy promotion. Although iron is usually the most effective metal to perform Fenton's reaction, the viability of non-Fe-based materials have been assessed as well.

Carbon felt is probably the most widely employed substrate to support Fe-rich structures, as shown for iron oxides like Co-Fe₃O₄ [403] or layered double hydroxides (LDHs) [404]. In cases like the former, the obtention of core-shells in which the iron compound constitutes the core

has been demonstrated to be a smart way to enhance the stability because of the minimization of iron leaching. On the other hand, 2D nanomaterials like LDHs are attracting much attention due to the greater exposure of most of the active sites to the generated H₂O₂, thus making unnecessary its diffusion through complex pore structures typical of 3D materials. Alternatively, carbon aerogels are proposed as more advanced supports for particles like iron sulfides [405]. Catalytic reactive membranes, also known as reactive filters, have become another appealing option to carry out the heterogeneous EF and related processes, since the integration of filtration and oxidation phenomena in a single element may simplify the more classical 2-step technology. Surface catalysis at filtration membranes may solve shortcomings like aggregation and deactivation of suspended catalysts and fouling of unmodified membranes. Moreover, the filtration process is expected to increase the direct mass transport of organic molecules and the H₂O₂ towards the coated catalyst, eventually favoring the oxidation events with the $\bullet\text{OH}$. Plakas et al. [406] manufactured a ceramic membrane loaded with Fe₃O₄ to perform a non-electrochemical heterogeneous Fenton treatment. When the catalytic membranes act also as one of the cell electrodes, in particular the cathode, they simultaneously serve as H₂O₂ source and its in situ decomposition via Fenton's reaction, as demonstrated using Fe³⁺ anchored on a PVDF microfiltration membrane [407].

Regarding the suspended heterogeneous catalysts, many examples have been published related to iron oxides [375,389]. Depending on the reactor design, the suspended oxides may be considered a catalytic particle electrode, which gives rise to a 3D heterogeneous EF system as discussed for magnetic Fe₃O₄-loaded N-doped reduced graphene oxide [408]. Less conventional but highly interesting are the treatments made with iron sulfides. In particular, the pyrite-catalyzed heterogeneous EF process has been described as a very effective method [409]. Natural pyrite is an excellent electron donor, and its S₂²⁻ transformation into sulfate occurs synchronously with Fe²⁺ and H⁺ release. Based on this, two degradation routes coexist: (i) conventional Fenton's reaction favored by the gradual acidification and (ii) heterogeneous Fenton's reaction. A serious concern of this system is the excessive iron leaching, which limits the catalyst reusability. Chalcopyrite (CuFeS₂) is another useful mineral to perform heterogeneous EF and PEF [410]. The presence of Cu(I), either in solid state or in solution upon leaching or dissolution, allowed the $\bullet\text{OH}$ production via a Fenton-like reaction with H₂O₂ and also regenerated the Fe(III), leading to the complete removal of cephalixin. Moreover, it was shown that the combination of pyrite or chalcopyrite with pressurized air can lead to very high TOC removals when treating synthetic solutions of caffeic acid and 3-chlorophenol [411].

Lately, highly porous Fe-based MOFs with abundance of active iron sites, tunable morphology and good Fe(III) to Fe(II) conversion have been designed as potentially better catalysts in Fenton-based advanced oxidation processes [293]. Among them, MIL-type (Materials Institute Lavoisier) structures exhibit an extraordinary catalytic performance for the degradation of organic pollutants. In some of them, the presence of unsaturated open iron sites allows the adsorption of H₂O₂. If this occurs in concomitance with a great electron donation from electron-rich ligands to Fe(III) centers, the Fe(II) regeneration is favored [412]. Likewise, the presence of electrophilic groups in the organic linkers reduces the electron density of the Fe(III) centers, which are then more easily converted to Fe(II). All this being true, raw MOFs not always are candidates to perform the heterogeneous EF treatment because the organic backbone suffers from gradual oxidation in such aggressive oxidizing conditions. In contrast, they have been shown very effective once pyrolyzed, since the resulting Fe-loaded porous carbons are much more stable. Pioneer works on this topic by Ye et al. are a benchmark for EF and related treatments. Synthetic pyrite NPs were synthesized by simultaneous carbonization and sulfidation of a 3D Fe-MOF. As can be seen in Fig. 27a, a core-shell FeS₂/C nanocatalyst was obtained. This material (0.4 g L⁻¹) led to the complete removal of fluoxetine spiked into urban wastewater by means of heterogeneous EF at pH 6.0 (Fig. 27a')

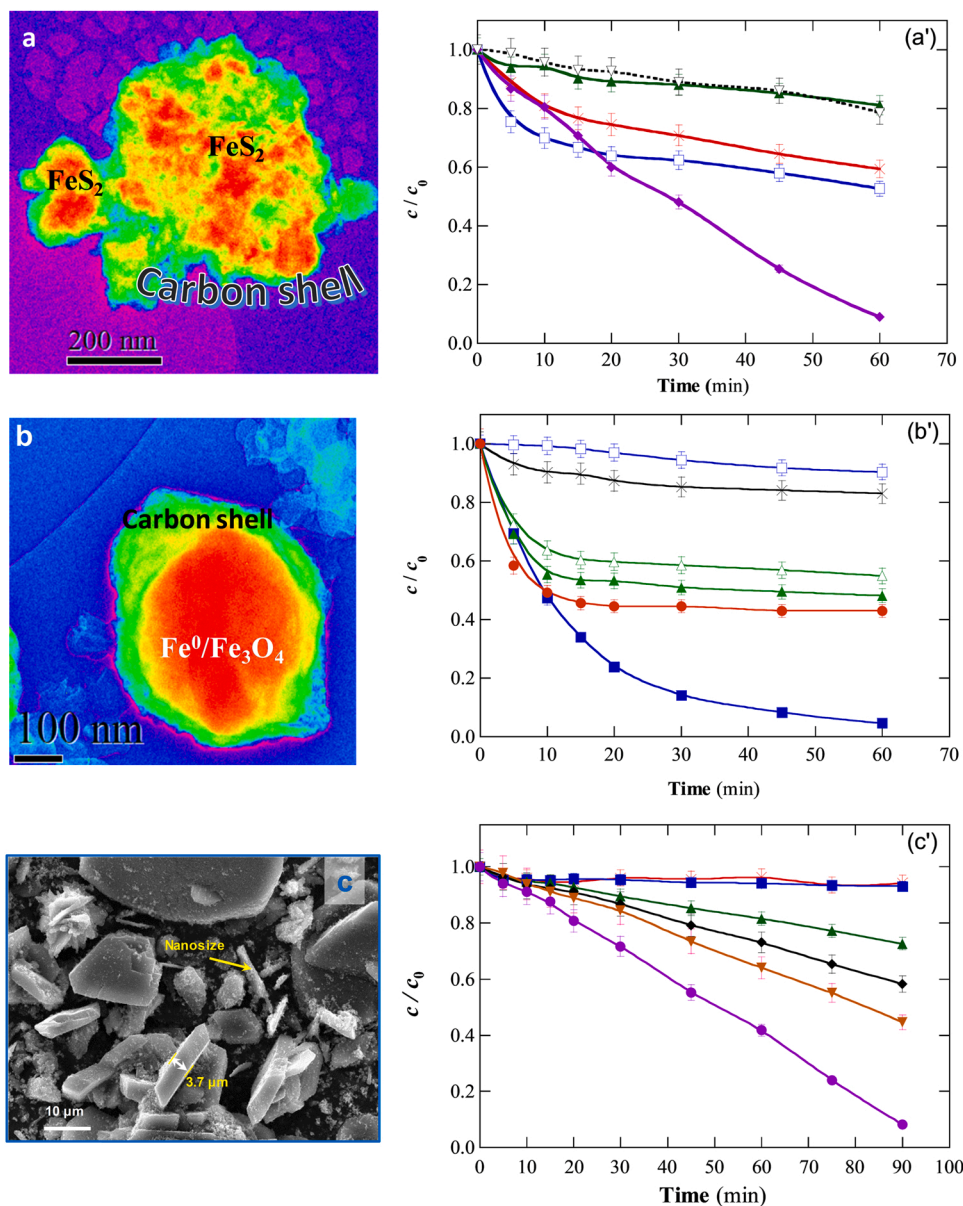


Fig. 27. Microscopic analysis of raw and pyrolyzed Fe-MOFs, and their performance as suspended catalysts for the heterogeneous Fenton-based treatment of 150 mL of aqueous solutions containing pharmaceutical micro-pollutants using a GDE/DSA electrochemical cell. (a) TEM image of a core-shell FeS₂/C nanocatalyst synthesized via pyrolysis at 400 °C; (a') the fastest degradation of 0.049 mM fluoxetine (i.e., 10 mg L⁻¹ TOC) spiked into urban wastewater at pH 6.0 was achieved by heterogeneous EF, causing its complete removal after 60 min at 50 mA using 0.4 g L⁻¹ catalyst. (b) TEM image of a magnetic core-shell nano-ZVI/Fe₃O₄@C-N catalyst synthesized via pyrolysis at 800 °C; (b') the fastest degradation of 10 mg L⁻¹ gemfibrozil spiked into a 0.050 M Na₂SO₄ solution at pH 5.5 was achieved by heterogeneous EF, causing its complete removal after 60 min at 50 mA using 0.2 g L⁻¹ catalyst. (c) FESEM image of a raw Fe-bpydc 2D MOF at 1000 ×; (c') the fastest degradation of 0.044 mM bezafibrate (i.e., 10 mg L⁻¹ TOC) spiked into a 0.050 M Na₂SO₄ solution at pH 5.1 was achieved by heterogeneous UV/Vis PEF, causing its almost complete removal after 90 min at 100 mA using only 0.05 g L⁻¹ catalyst. (a) Adapted with permission from [412]. Copyright 2020 ACS. (b) Adapted with permission from [413]. Copyright 2020 Elsevier. (c) Adapted with permission from [414]. Copyright 2020 Elsevier.

[412]. In a second study, a magnetic core-shell nano-ZVI/Fe₃O₄@C-N catalyst was synthesized via pyrolysis at 800 °C (Fig. 27b). The fastest degradation of 10 mg L⁻¹ gemfibrozil spiked into a 0.050 M Na₂SO₄ solution at pH 5.5 was attained by heterogeneous EF with 0.2 g L⁻¹ catalyst (Fig. 27b') [413].

An interesting exception to the presumed low stability of the raw MOFs is presented in Fig. 27c, which shows an Fe-bpydc 2D MOF. The fastest degradation of 0.044 mM bezafibrate spiked into a 0.050 M Na₂SO₄ solution at pH 5.1 was achieved by heterogeneous UV/Vis PEF using only 0.05 g L⁻¹ catalyst (Fig. 27c') [414]. In this latter example, the presence of carboxylic groups in the ligand enhanced the stability against hydrolysis.

Note that when using suspended catalysts, particle aggregation negatively affects the •OH productivity. In addition, the final separation/recovery post-treatment may be costly and slow. Catalyst loss increases the treatment cost and is detrimental for water quality.

4.2.9.4. Reactors at different scales. As in all electrochemical processes, an adequate reactor design is essential in environmental electrochemistry to achieve both, a suitable potential and current distribution that

maximizes the electrode lifetime and its selectivity toward the target reactions, and an excellent hydrodynamics that reduces the treatment time upon perfect mixing of the Fenton's reagents. The most typically used cells for carrying out the EF and related treatments explained in this subsection are bench-scale stirred tank reactors with a maximum capacity of 1 L (i.e., thermostated beakers with a magnetic follower to ensure the mass transport). Apart from these, some unconventional cells have been employed at this scale: (i) Systems with immersed cathodes like carbon felt in which the aeration is made directly thorough the submerged part of the electrode surface, aiming to enhance the H₂O₂ production and Fe²⁺ reduction [415]; (ii) tubular reactors with a GDE [416]; (iii) rotating Fe₃O₄/GDE disks [417]; and (iv) pressurized cells for EF and PEF [418].

However, investigation at larger scale is needed in order to corroborate the results obtained at small scale, as well as to identify the major constraints that constitute a current barrier for full-scale deployment. Bigger systems to treat up to 10 L in batch to recirculation operation mode are rare, but they provide crucial information. The experimental setups involve the use of purpose-made filter-press cells. A representative example is the evolution of the SPEF process devised by Brillas and

co-workers, which started from a 2.5-L pre-pilot plant that performed well for the treatment of organic pollutants in urban wastewater even at low input current [233]. Then, a 6-L plant that included a filter-press cell with a 3D GDE was run for treating levofloxacin solutions. A parametric model served to simulate the TOC decay vs. time [419]. A similar plant with a bigger capacity (10 L) and a carbon-felt cathode allowed the total removal of erythromycin (100 mg L^{-1}) [420]. At present, the largest plant to test the SPEF process is located at the Plataforma Solar de Almería (Spain) (Fig. 28). The electrochemical part consists of four commercial plate-and-frame cells, each one equipped with a GDE (100 cm^2) and a Nb/BDD mesh as the cathode and anode, respectively. This system has capacity to treat up to 100 L, and its ability to degrade several pesticides in a mixture was recently reported [421]. In addition, endurance tests were carried out to evaluate the durability of the GDE [422].

The transition from batch mode to continuous-flow reactors has been far less explored. This is a drawback of this group of technologies because operation in continuous mode is required in some applications, especially when large volumes are to be treated and cannot be stored for long time in the facility (e.g., wastewater treatment plants). One of the few available examples is based on the use of a flow-through reactor developed by Zhou [400]. This type of reactor is more efficient than those operating in flow-by mode, requiring lower energy consumption for degradation.

As described above, also the combination of several microreactors in series has recently been addressed to evaluate the EF treatment in continuous mode. On the other hand, a recent patent [423] reports a tubular water-processing reactor with DSA and GDE as the anode and cathode. It was operated in continuous mode, ensuring the accumulation of H_2O_2 , a good percentage of Fe^{2+} regeneration and the complete degradation of benzotriazole in different water matrices, which are promising results for further upscaling.

4.3. Persulfate reduction to sulfate radical anion

4.3.1. Purely cathodic process

Although the $\cdot\text{OH}$ -based AOPs are recognized as the most powerful tools for advanced water treatment, the $\text{SO}_4^{\cdot-}$ -based AOPs are emerging as a strong alternative or complement to degrade organic pollutants, since $\text{SO}_4^{\cdot-}$ is a bit less powerful ($E^0(\text{SO}_4^{\cdot-}|\text{SO}_4^{2-}) \sim 2.4 \text{ V} < E^0(\cdot\text{OH}|\text{H}_2\text{O}) = \sim 2.7 \text{ V}$, both vs. SHE) [424] but much more stable (i.e., half-life of $30\text{--}40 \mu\text{s}$ vs. $0.02 \mu\text{s}$) [425] radical than $\cdot\text{OH}$, being possible to maintain the performance of the treatment for longer time.

The anodic production of sulfate radical anion ($\text{SO}_4^{\cdot-}$) is feasible from sulfate oxidation at large O_2 -overpotential anodes like BDD, as has been commented in previous Section 2. Conversely, less attention has been paid to its direct cathodic production. There is no doubt that this is a minor reduction route as compared with ORR to H_2O_2 , but it is inherently valuable and deserves further study because it is a straightforward manner of producing a very powerful oxidant, unlike the case of ORR.

Peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$), routinely called persulfate, can be either added as chemical or produced at the anode to be employed as a strong oxidant against many organic pollutants. Nonetheless, it is more effective once transformed into $\text{SO}_4^{\cdot-}$, which is possible through many routes, as for example cathodic reduction at certain electrocatalytic surfaces via reaction (54) [426]. For instance, the authors of various publications hypothesized the direct reduction of PDS at Pt [427] or glassy carbon [428] cathodes, although they did not give clear evidence of such phenomenon. In a couple of detailed studies, the cathodic PDS reduction to $\text{SO}_4^{\cdot-}$ was evidenced from the irreversible peaks obtained during the voltammetric analysis performed with Pt, graphite and Fe_3O_4 -modified glassy carbon working electrodes [429,430]. In contrast, other works refer the nonradical cathodic activation of PDS [431].



Based on these results, the electrochemical (i.e., cathodic) activation

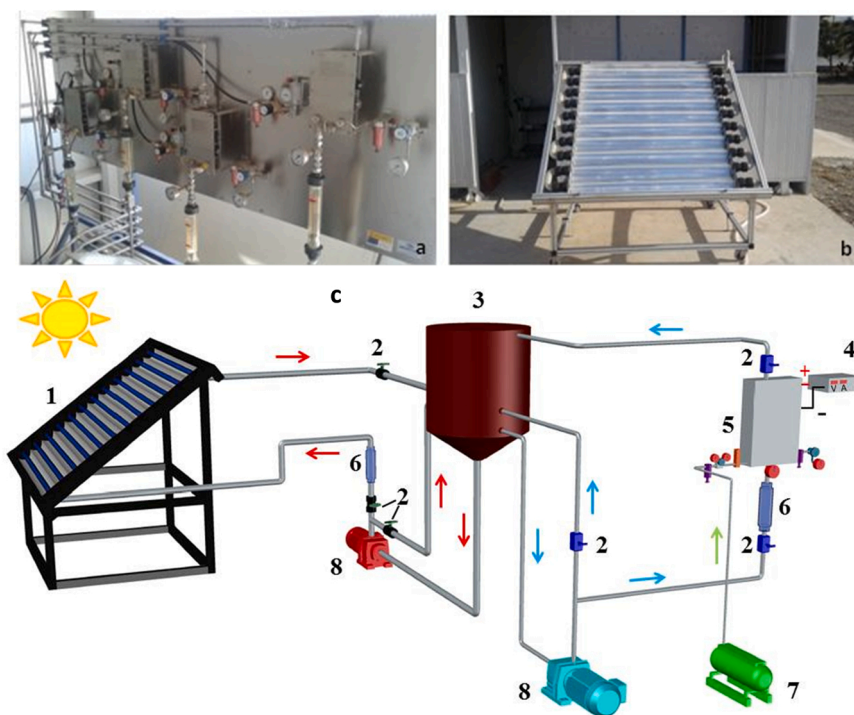


Fig. 28. Front view of (a) the four filter-press type electrochemical cells of the pilot unit, and (b) the CPC photoreactor. In (c), sketch of the pilot unit equipped with one cell (examined in this work), showing the different elements: CPC photoreactor (1), valve (2), solution reservoir (3), power supply (4), electrochemical reactor (5), liquid flowmeter, (6), air compressor (7), magnetic recirculation pump (8). Adapted with permission from [421]. Copyright 2019 Elsevier.

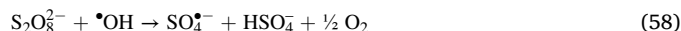
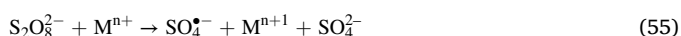
of persulfate (referred as EAP) could become an interesting strategy to be integrated with anodic processes for water treatment. However, more progress is needed to achieve higher mass production rates that make the process worth testing at larger scale. Within this context, the electron transfer from the electrode would be enhanced by leveraging the wide range of cheap three-dimensional carbonaceous materials that could expose a greater surface area for reaction (54). This, combined with their modification with suitable electrocatalysts like iron-based materials that proved particularly active, could definitely boost the $\text{SO}_4^{\bullet-}$ production [432].

4.3.2. Coupling strategies based on $\text{SO}_4^{\bullet-}$ production

Although some few incipient works have been devoted to investigate this type of coupling, the field is still underdeveloped but shows good perspectives to become fertile. The first possible combination that is worth commenting but has never been tested, as far as we know, would involve the simultaneous production of cathodic $\text{SO}_4^{\bullet-}$ via reaction (54) and anodic oxidants like $\text{M}(\bullet\text{OH})$, $\text{S}_2\text{O}_8^{2-}$, $\text{SO}_4^{\bullet-}$ and active chlorine (see their production in Section 2). Ideally, there would be no need of persulfate addition, since it can be generated in situ from sulfate oxidation at certain anodes like BDD. This could then become a close-loop approach, in which the cathodic $\text{SO}_4^{\bullet-}$ production is self-sustained by the anodic reaction.

Two other strategies related with the $\text{SO}_4^{\bullet-}$ production have been discussed in the literature. They are not based on direct PDS reduction at the cathode, but on its chemical transformation through electro(re) generated activators. One of them is based on the catalytic decomposition of PDS in the presence of low valence transition metal ions (M^{n+}) [426], such as Fe^{2+} [433,434], via reaction (55). In conventional activation, the production rate of $\text{SO}_4^{\bullet-}$ decreases over time because of the gradual accumulation of the less active form M^{n+1} . The electrochemistry offers a solution to this problem by promoting the cathodic regeneration of M^{n+} , especially upon use of three-dimensional cathodes. This was recently shown employing a cell with a carbon-felt cathode, which stimulated the continuous regeneration of Fe^{2+} (initially added at a concentration as low as 0.2 mM) as soon as it reacted with 5.0 mM PDS added to a bisphenol A solution [433]. The superiority of the porous cathode over a planar stainless-steel electrode was evidenced. Since in aqueous media, $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ coexist, additional experiments performed in the presence and absence of radical scavengers revealed the main role of $\text{SO}_4^{\bullet-}$, as compared to $\bullet\text{OH}$, to degrade the organic pollutant. Furthermore, both radicals acted synergistically with active chlorine produced anodically at a DSA plate, thus constituting a highly oxidizing system. Note that in this first strategy, an excess of M^{n+} must be avoided because it deactivates the $\text{SO}_4^{\bullet-}$ through the parasitic reaction (56).

The second possibility consists in the mutual decomposition of PDS and H_2O_2 to yield their respective radicals, as shown in reaction (57). This is again interesting to be implemented in an electrochemical cell because H_2O_2 can be cathodically electrogenerated as explained in subsection 4.2. This option was tested using added PDS and a GDE as cathode in a stirred-tank reactor, leading to almost complete decolorization of a dye solution and 71% mineralization after 360 min at 33.3 mA cm^{-2} [435]. In addition, in all the experiments with PDS a slight rise in temperature (up to 45–50 °C) is advisable because its thermal activation can also yield some $\text{SO}_4^{\bullet-}$. In this system, as it occurs in all degradation studies with PDS, the cogenerated $\bullet\text{OH}$ can act as activator according to reaction (58), which enhances the overall performance. Alternatively, if Fe^{2+} is added as H_2O_2 is electrogenerated, the occurrence of Fenton's reaction (see subsection 4.2.3) would also be a source of $\bullet\text{OH}$ that could participate in reaction (58). Finally, anodic water oxidation can also serve as a source of $\text{M}(\bullet\text{OH})$, which may act either directly onto the organic molecules or react with PDS to yield $\text{SO}_4^{\bullet-}$, as discussed for a BDD/carbon felt cell [435].



Note that, in the context of process coupling, both cases of chemical PDS activation (i.e., via M^{n+} or H_2O_2) could further benefit from the in situ anodic production of PDS, an option that merits to be further exploited.

4.4. Perspectives and further innovations on coupled redox processes

Frequently, the choice of a specific purely anodic or cathodic process and of a cell configuration for the degradation of organic pollutants is a trade-off between efficiency and effectiveness. Conversely, several arrangements can be individuated to address the same environmental challenges by means of coupled redox processes that allow operating with both, high effectiveness and efficiency. In our last review, we concluded that the prospects of advanced electrochemical methods for the treatment of organic contaminants of emerging concern in water seemed bright and, in particular, the coupled redox processes were going to gain momentum. However, the full-scale deployment of these technologies still demanded the development of optimum but relatively cheap and stable catalysts, cathode materials and reactors. Great attention has been paid to all these aspects, although still the following considerations can be singled out in order to facilitate the excellent scale-up perspectives:

- i) In coupled processes that involve direct ER, future advances should be related to the use of novel and more efficient cathodes, and the treatments could be partly oriented towards the removal of specific functional groups that are more directly correlated to a high biorecalcitrance. Modulated electrolysis, requiring the continuous monitoring and re-adjustment of I_{appl} or E_{cath} , would allow working at the highest Faradaic efficiency, which could be feasible in practice using a tethered programmable constant-current or constant-potential power supply or potentiostat. The coupling between the electrochemical step and a biological post-treatment should also be further studied and optimized. In addition, the formation of reduction intermediates and their possible re-oxidation products must be assessed in real water matrices;
- ii) In coupled processes that are based on the cathodic H_2O_2 production, the stability of such production needs to be assessed, in order to find out the lifetime of the cathodes, elucidate the degradation mechanisms and find viable solutions to mitigate the loss of performance or demonstrate through an economic evaluation that the operation and maintenance expenses are affordable. To this purpose, long-term electrolytic trials at pilot scale are required, with special emphasis in testing of promising biomass-derived carbons;
- iii) SACs and other atomic-scale electrocatalysts have emerged in the last lustrum as ideal materials that can be fine-tuned to perform reactions like the two-electron ORR with outstanding current efficiency. This has been demonstrated at small scale in very clean environments but, for practical upscaling, their stability upon prolonged electrolysis, in pilot plants and using actual wastewater matrices is almost unknown and merits further investigation;
- iv) Pumpless systems to avoid the air compressor are also under investigation for H_2O_2 production, since they would represent a significant cost reduction. Cathodes like FACs and NADEs, as well as reactors based on the Venturi effect, high pressure, minimum inter-electrode distance or smart collection of the anodic O_2 have been proposed so far, but further insights are needed. The

ultimate goal could consist in devising autonomous systems with high energy efficiency;

- v) As mentioned above, the direct cathodic $\text{SO}_4^{\bullet-}$ production can be plausibly coupled to the in situ generation of strong oxidants. Additionally, the cathodic H_2O_2 cogeneration and Fe^{2+} regeneration can be attempted as well, thus reinforcing the degradation upon the combined action of multiple radical species;
- vi) In homogeneous Fenton-based EAOPs at circumneutral pH, iron chelators as soluble catalysts should be highly active to react in a quick manner with H_2O_2 , but sufficiently stable to minimize their degradation and the subsequent iron precipitation. Most of the currently used catalysts can only satisfy one of these two requirements;
- vii) In heterogeneous Fenton-based EAOPs at circumneutral pH, there is a need of catalyst recyclability tests in actual wastewater. In addition, the development of effective heterogeneous catalysts at very low concentrations is of interest because of the lower treatment cost and the minimization of the sludge production. Carbon-supported electrocatalysts with protective shells, made from the pyrolysis of highly porous MOFs, can be established as stable multifunctional platforms that allow the occurrence of several phenomena: adsorption, filtration, homogeneous and heterogeneous catalysis, electrocatalysis and even photocatalysis;
- viii) Nano- and micromaterials that are employed as suspended catalysts for heterogeneous Fenton's reaction seem preferable because supported catalysts on the cathode surface may hamper the two-electron ORR, inducing instability and lack of reproducibility, and diminishing the exposed surface area for H_2O_2 production. For nanocatalysts, it is interesting to confer magnetic properties, so that the final separation and recovery becomes easier;
- ix) Lately, modified electroactive membranes (i.e., reactive filters or electrified membranes) are being developed for combined filtration and heterogeneous Fenton-based EAOPs. Most of the tested systems for such integration of technologies rely on polymer membranes, but it is recommended to perform tests with newly-developed catalytic ceramic and MMO membranes due to their outstanding characteristics for industrial implementation [436, 437];
- x) As a last remark, it must be highlighted that there is huge need for operation of reactors in real environments, which would provide data for a consistent techno-economic analysis and the development of viable business models. The penetration of the reviewed coupled processes into the market should be sustained by a series of case studies that finally constitute a wide and robust portfolio.

Based on all these remarks, it can be concluded that the coupled processes are emerging as a new area of opportunities. If significant advances are achieved once these aspects are addressed, some of the reviewed systems will become a strong competitor with very appealing features, in good agreement with new policies on sustainability, circular economy and independence from scarce raw materials.

5. Scale-up of electrochemical processes for the degradation of organic water pollutants

As explained in previous sections, hundreds of works have been published in the last three decades, with a remarkable growth in the last six years, regarding the potential use of electrochemical technologies for the treatment of wastewater containing organic contaminants [60, 438–440]. The promise of a fast application was associated to many of these technologies since the very beginning in the earliest seventies, but the reality differs dramatically from that position, even nowadays, more than half a century later [439]. New concepts such as the TRL scale have arisen and help to understand which is the real situation and which

actions should be taken in order to go forward in the development of applications [73].

5.1. The climate-water-energy nexus

Public backlash against unregulated or uncontrolled environmental pollution is one of the most evident social concerns nowadays. Climate and environmental challenges can be streamlined by means of smart coupling between anodic and cathodic processes, thus turning the new water policies being released worldwide into opportunities that allow upscaling of electrochemical systems with proven effectiveness at smaller scales. As an example, new policies on wastewater reuse for irrigation, especially in agriculture, demand that disinfection and removal of organic micropollutants is ensured to become a safe strategy able to protect for as long as possible the natural freshwater resources that are currently used for such purpose. The electrochemical technologies reviewed in this section can be considered a viable approach, since the different oxidants that are produced cathodically and anodically can be directly employed for disinfection or be further activated to address the destruction of the most stable organic pollutants and microorganisms. Within this context, it will then be necessary to carry out demonstrations at large scale using actual wastewater effluents, as well as to show the impact of the treated water on the different crops, plants and even the soil properties and microbiota.

On the other hand, decarbonisation strategies are being planned to limit global warming, in good agreement with the Global Climate Agreements like the Paris Agreement. At the same time, estimates reported by the International Energy Agency (IEA) predict a rise in the global energy demand by 25%–30% by 2040. Regarding these two key issues, there exists a stimulus plan for energy transition and the electrification of society, which is forecast to lead to the advent of the hydrogen economy. Hydrogen could become the energy vector of the future, replacing combustion engines to finally decrease the toxic emissions. The hydrogen production costs will fall by 50% by 2030, according to the World Energy Council, which could reach even lower prices if it was cogenerated in coupled water treatment processes. Innovations on coupled electrochemical redox processes within this context could give more relevance to green hydrogen production systems, as follows.

- i) Cathodic H_2 production coupled to direct or mediated oxidation of organic pollutants or wastewater reviewed in Sections 2 and 3. Therefore, H_2 evolution would become a side reaction with value-added instead of a worthless phenomenon [187,441,442]. Other sources of green H_2 , not addressed here, are: biofuel cells (i.e., bio-oxidation of organics), photoelectrochemical cells (i.e., photo-oxidation of organics) and electrocoagulation (i.e., anodic production of coagulant precursors);
- ii) Cathodic H_2 production coupled to the oxidation of industrial organic surplus, as in the case of glycerol, whose oxidation occurs at a lower potential than water, thus diminishing the cell voltage (i.e., the energy consumption for H_2 consumption) as compared to conventional electrolyzers [443];
- iii) Cathodic H_2 production coupled to $\text{SO}_4^{\bullet-}$ electrogeneration at a large O_2 -overpotential anode like BDD [444].

Clean energy from renewable sources gives rise to wind-driven or sunlight-driven (for both, sun-assisted reactivity and sun-power device functioning) electrochemical systems, which could be an interesting option for operating the coupled processes described in Section 4. There exist unconventional energy sources as well, as exemplified in the H_2O_2 production at a GDE coupled with a photoanode, where current was supplied from a RED device (see sub-Section 3.3.2 [258,445,446]), or the so-called triboelectric generators to power EF treatment [447,448].

Direct decarbonisation, with cathodic transformation of CO_2 (i.e., CO_2 reduction reaction (CO_2RR)) into value-added chemicals,

represents another process that can be integrated in coupled redox systems in which the oxidation of organic pollutants might take place at the anode. Ideally, the organic pollutants could be mineralized up to CO_2 , which would be the source for the CO_2RR in a close-loop system. Divided cells are needed to both accumulate the cathodic products to be recovered and prevent their contamination and re-oxidation, as shown for the CO_2 conversion to formic acid using a tin cathode [188,449]. As recently reviewed by Vass et al. [449], it is necessary to make a deep screening of anode processes that could be coupled to the CO_2RR , which can be challenging. Some authors state that the EO of alcohols can be paired with the CO_2RR [279], which opens the doors to a similar strategy to that mentioned above for glycerol-mediated H_2 production.

Based on these examples, it can be stated that the link between electrochemical water treatment and decarbonisation strategies is rather strong. To further support the correlation, note that this has been recently quantified within the context of drinking water treatment, demonstrating that carbon emissions in the sector will be reduced, with more intensity as the electricity grid becomes greener in the near future [450].

5.2. Why is it convenient to use equipment of different sizes for the electrochemical treatment of organics?

Typically, scale-up theory differentiates between several types of scale studies during the evaluation of processes using iconic physical modelling, ranging from the lab-scale to the full-scale. Although depending on the academic reference, different classifications can be found, it can be assumed that lab, bench, pilot and prototype can be the four steps to be fulfilled along the way towards the full understanding and characterization of a process. Typically, the size of the setups increases according to that step sequence and, because of that, there is a general misunderstanding regarding the size-scale relationship, being sometimes assumed by many researchers that the difference between a lab or a pilot scale is simply based on the size. However, it is important to bear in mind that differences are not in the size but in the purpose of the study carried out, that is, in the information that aims to be drawn from the specific experimental device.

In the context of this review, the development of electrochemical technology for the treatment of wastewater can be distinguished according to the purpose of the work, and two cases are worth to be highlighted: (i) Applicability of the electrochemical technology to the treatment of different types of wastewater; and (ii) development of electrochemical cells, referred either to single components or to the whole mechanical design. The first cases are typically studied by chemist and chemical engineers, whereas the second ones are carried out by chemical or mechanical engineers.

5.2.1. Lab-scale devices

These are used for preliminary evaluation in which the technical viability of a process and kinetic or thermodynamic data are investigated. It is the stage at which, for example, different electrode coatings may be compared or at which the effect of anions such as sulfate or chloride on the degradation of an organic pollutant is characterized [451–453]. Synthetic solutions instead of wastewater allow in this stage to obtain accurate measurements and to draw theoretical conclusions on the fundamentals of the processes, without masking effects coming from the multiple inputs that are typically found when working with actual wastewater [454]. A very important characterization, both from the electrochemical and analytical points of view (voltammetry, impedance, characterization of reaction intermediates, etc.), is needed at this level to succeed, as discussed in our previous review [1] and in Section 2.3. In the last years, the development of new MMO coatings [68,147,455], the evaluation of the degradation of anthropogenic pollutants in the presence of controlled electrolytes [456–458] or the disinfection of different types of pathogens [32,459] were the key topics, giving rise to a very extensive production of scientific knowledge (as discussed in Section 2).

5.2.2. Bench-scale devices

This represents a step forward, in which flow patterns and integration with other auxiliary processes are evaluated, but still using lab-scale materials and under very controlled conditions. Instead of pure solutions of pollutants, the formulation of synthetic wastes tries to approach to the parameters of actual wastewater [460,461] and in the most advanced phases of this stage, real wastes can be used [462–467]. The effect of operation parameters (e.g., temperature, current intensity) on the process performance [468], the combination with other processes (e.g., UV photolysis, ozonation), the comparison between discontinuous and continuous operation modes, the effect of flow patterns [469] and preliminary stacking are some of the targets of these studies [470,471], as discussed in Section 2.3. Preliminary figures of merit can be obtained, as well as a preliminary idea about the practical operation of the process [467,472]. Laboratory materials and equipment are still often used at this scale (e.g., industrial water streams for cooling or steam for heating are not employed yet, gases are not managed but they are simply dissipated, no important worries about connection of power supplies with electrodes are detected), and mechanical design is still far from the target, although there are many works in which commercial cells ready for implementation in full-scale applications are used. Connections between the cell and the power supply are made with a simple technology, like that at lab scale, and instrumentation corresponds to that of a conventional research laboratory. Heating/cooling devices, power supplies and even cells can be the same as those used at lab scale. Because of that, the analytical and electrochemical characterization techniques become less essential than at lab scale [473]. A very interesting aspect at this stage is to evaluate if the small electrodes tested in the lab-scale studies can be significantly enlarged without suffering a significant loss of performance or stability. Also, reproducibility tests can be carried out with these larger size electrodes [474]. However, in the last years, the most significant efforts at this scale have been focused on the combination of electrochemical processes with other AOPs [438], as is the case of photoelectrolysis, sonoelectrolysis and electrochemically-assisted Fenton or ozonation processes [475,476]. The most advanced of these studies compare the performance in continuous and discontinuous operation modes. Also, the testing of actual wastewater with small cells (equipped with electrodes whose geometric areas are typically up to 100 cm^2) are found in the literature as representative of bench-scale studies. Many of these works attempt to upscale the system to the pilot level, trying to approach the guidelines of what should be the real application according to the experience gained [467,472,477], eventually solving the main problems associated to the use of this actual waste.

5.2.3. Pilot-scale devices

In this context, the use of commercial cells or in-house cells made with the expected materials in full-scale application for the manufacturing of the cell (including not only electrodes or membranes but also the frames), the incorporation of industrial equipment for all the auxiliary units that will be connected to the electrochemical cell and the treatment of actual wastewater instead of synthetic solutions are several of the targets of the pilot scale studies [193,478]. There is a lot of work to be done for the development of efficient electrochemical cells, as pointed out in recent critical reviews focused on the bipolar trickle tower reactors [479] and planar parallel flow channel cells [191]. Also, the use of novel techniques such as the 3D printing to produce tailored electrodes with outstanding properties [480] or the development of 3D electrodes can perfectly lead to the design of efficient electrochemical cells [481,482]. As the size of the electrodes compromises the obtention of uniform current distribution, the stacking of cells becomes a critical point in this stage [483,484]. However, studies regarding stacking are much less common than in other electrochemistry fields such as the fuel cells or electrolyzers for the production of hydrogen [73,485,486], and even less numerous than in a pretty much incipient topic like bio-electrochemistry [487] or reverse electrodialysis [488]. Also, it is

important at this stage to address the real mechanical design of the cell, that from here should look for cells produced industrially in series and less for in-house made cells. Elements such as gaskets or current distributors become critical to reach good results and they may have a relevance that can be even higher than that of the electrode composition [489]. The type of pumping device (e.g., centrifugal, alternative), the equipment for heat exchanging, the need of venting and gas management are relevant factors at this stage, although, unfortunately, they are not the target of most of the scientific works. Concerns about the quality of reagents arise, trying to minimize the operation cost (e.g., for regulation of pH, reagents should not be of laboratory quality, but rather of industrial/technical grade). The placement of the elements of the plant is also important, as it affects key aspects such as heat dissipation and safety issues. Fouling of electrodes or membranes, or even of pipes, not only because of the expected reactivity but also because of external components of the wastewater, is also a point to be considered [490, 491]. Also, a complete list of operation problems is expected to arise from these studies but, once again, these factors are absent in the published literature regarding the electrochemical degradation of organic water pollutants, as also occurs with many other relevant issues that are only starting to appear in recent papers [225]. Also, technicians are lacking valid figures of merit that can help to carry out a rough economic estimation of the given treatment [492]. In addition, it is important to make progress on the automatization, throughout the development of control strategies that allow all equipment to operate in a coordinated mode [493].

Hence, although the term “scale up” literally means “size increase”, other considerations have gained importance in recent years, aiming to be more informative on the real applicability of upscaled systems [494]. There are hundreds of examples of studies made at the different levels in recent years, but very few information available in the scientific literature regarding the higher scales. In the near future, new challenges that complement both, the exhaustive evaluation of the influence of the operation parameters and the performance of different processes when treating different organic pollutants or wastewaters matrices, must be addressed. The results from such studies can have even more relevance to reach the highest efficiencies in the electrochemical treatments not only of those related to the degradation of organic pollutants but also to other related processes like electrocoagulation [192,495,496]. Among them, inputs widely evaluated for industrial applications, which are currently in operation, are started to be targeted in electrochemical wastewater treatment. One of the most relevant is the mechanical design of the cell, which has been evaluated exhaustively for incipient technologies such as the microbial fuel cells [497] but, unfortunately, is not as widely studied for the processes reviewed in this paper. Significant outcome is expected from this kind of research [485,498]:

- Current density distribution, which affects to the maximum admissible size of the electrode and may have a dramatic impact on the efficiency and even on product distribution (as indicated in Section 2.3 for lab scale cells). This effect is widely studied in fuel cells and electrolyzers but almost rarely addressed in electrochemical wastewater treatment [499];
- The flow patterns (i.e., fluid dynamics) and the reduction of the inter-electrode gap, which may help to decrease the cell voltage and hence, the energy consumption [439,479];
- Current feeders, that is, the electric connections between the cell and the power supply and in which highly imaginative solutions are being recently proposed, such as contactless energy transfer Integrated magnetics structure like current double rectifier (CDR) [500].

Other aspects that remain unsolved are: (i) The gas management; (ii) the necessity of auxiliary equipment; and (iii) the regulation of I_{appl} . Regarding the first aspect, most of the electrochemical treatments of wastewater involve the evolution of O_2 and H_2 associated to water oxidation and reduction, respectively. Oxygen does not entail any

relevant operation problem, although it provides visual information about the inefficiency of the system. In contrast, hydrogen can pose significant issues. For example, the application of 100 mA cm^{-2} in the EO process leads to the production of up to $0.4178 \text{ Nm}^3 \text{ h}^{-1} \text{ m}^{-2}$ area of hydrogen (data calculated for a 100% current efficiency for water reduction). In the case of a lab scale device with 15 cm^2 this means only 0.63 NL h^{-1} , but in the case of a pilot with a cathode area of 20 m^2 , the production can be as high as $8.36 \text{ Nm}^3 \text{ h}^{-1}$. Dissipation of the first is easy through the laboratory environment; the second may produce important problems if not properly managed [501]. As reviewed in Section 4.2, the cathodic production of H_2O_2 becomes an interesting alternative to prevent the hydrogen formation, but the concepts of existing cells are still far from real full scale and hence, the scale up of these complex reactions is tricky [299,328,353]. The use of divided cells and suitable dedicated pipelines for flowing the high-quality hydrogen for further valorization is widely suggested in many papers, but not seriously evaluated in the scientific literature (see some examples in Section 4.2). The increase in the operation cost and maintenance problems because of the rising cell voltage and fouling of the membrane, respectively, are considered as major challenges.

Regarding the supply of electric charge to the electrodes, studies about the effect of applied electrode potential may have sense from an exploratory point of view at the lab scale, trying to investigate on the electrode selectivity for a given reaction. However, the utilization of galvanostatic current supply is more suitable for greater scales. Moreover, results obtained in galvanostatic mode can also be misleading because of the simplification effect from the use of simple synthetic water matrices. Thus, in those systems the current is kept constant aiming to keep the same reaction rate found with simplified matrices, but this does not warrant that the oxidation of the required pollutant occurs as fast as expected. An alternative proposed in the literature tries to go further, maximizing the current efficiency by changing the energy supplied according to a scheduled trajectory (i.e., modulated electrolysis), which theoretically would allow harnessing the power supplied. However, this alternative is very recent, and a very exhaustive scale-up evaluation should be done to assess its feasibility [502].

Regarding the cell design, a very important set of studies are those based on the development of new cells [489], which are typically in the limit between bench and pilot depending on the purpose of the study. Some authors evaluate and/or modify some commercial cell [483,503], whereas others try to develop new components for a cell [490,503–508]. Typically, they need computational fluid dynamics (CFD) to obtain accurate understanding of the enhancements obtained with the modelling. In this context, mathematical modeling is a topic of major significance, which complements physical modelling (scale-up assessments) because it allows understanding better what happens during the application of the processes and how to optimize their performance [509–513]. Both, phenomenological and empirical models, need to be considered. First, in order to draw the master lines because they help to understand what is happening inside the cell [503,512] and, second, to reduce the complexity of the formulation in representing changes in very particular parameters. Good modelling works have been published in recent years with this goal, both for the development of cells [514] or applications [515]. However, after a comparison between the efforts in modelling in the electrochemical wastewater treatment and those in other fields of the electrochemical technology such as the energy field, one can realize that a much lower attention has been paid in the former case. And this is an evidence that contrasts with the outstanding work led by many groups, which provide pilot and high TRL data that need to be more deeply understood and modelled.

5.3. Towards more realistic electrochemical cells for the removal of organics

Perhaps, the most suitable strategy to scale up the EO processes should be the use of flow cells, which allow operating under different

circumstances [192,516,517]. For example, in intermittent or constant mode, either with single pass or batch flow. More control on the electrolyte or water matrices flow could be attained in the reaction compartment by using turbulence promoters as well as higher surface area/geometry/volume ratio and the stacking as multiple cells [26,56,191,192,516,517]. The classical plane parallel electrode geometry has been extensively incorporated to flow reactors due to many practical advantages. The reaction environment in these cells has been both experimentally and theoretically described, especially in relation to fluid flow, fluid dispersion, mass transfer, potential distribution, and concentration change. On the other hand, efficient flow-through and 3D flow-by electrodes in monopolar, bipolar or mixed arrangements [191,192,517] mathematical and computational fluid dynamics (CFD) calculations, prototype evaluation and simulation models can be also used “easily” to describe the reaction environment in accurate and quantitative profile [192,516].

Using flow reactors, several modifications are possible to reach the commercial scale according to the decontamination requirements [26,191,517]. For example, electrochemical systems coupled to an individual reservoir, flow modes by using gravity or peristaltic pumps as well as non-recirculating flow. Other options are the use of perpendicular or parallel electrodes arrangements, multi-plates arrangements evaluating the oxidants production at cathodic or anodic compartments, and zero-gap-electrode reactors could be also projected [26,517]. Different

electrocatalytic materials configuration inside the cells offer significant improvements on the performance of above flow reactors (3D, perforated and multi-plates) promoting homogenous mass transport and controlled turbulence effects as well as ease gas elimination and well-defined hydro- and fluidic- dynamics. Constant currents or current densities can be supplied to the electrodes in galvanostatic approach, estimating the electrical requirements and consequently, the economic costs. Another feature is that no tangible techno-economic information is obtained from the use of non-divided agitated beakers or non-divided stirred tanks, therefore, flow systems implementation is the best strategy to perform a suitable scale-up.

Regarding the electrodes, price, convenience, service life, maintenance supplies as well as the development of nanostructured materials to make available innovative substrates and catalysts are exciting trends and practical aspects that should be taken into consideration for the applicability EO-based technologies at large scale. For reaction compartment, zero-gap technology could allow to treat water matrices with low conductivity and optimizing the oxidants production. However, more studies are needed.

As illustrated in Fig. 29, the advances on the electrochemical reactors have been focused on electrochemical flow reactors. Another feature is that the most relevant developments to translate lab cells conditions (typical filter-press electrolyzers are used) to commercial units, have been achieved with diamond cells. It is mainly due to the higher

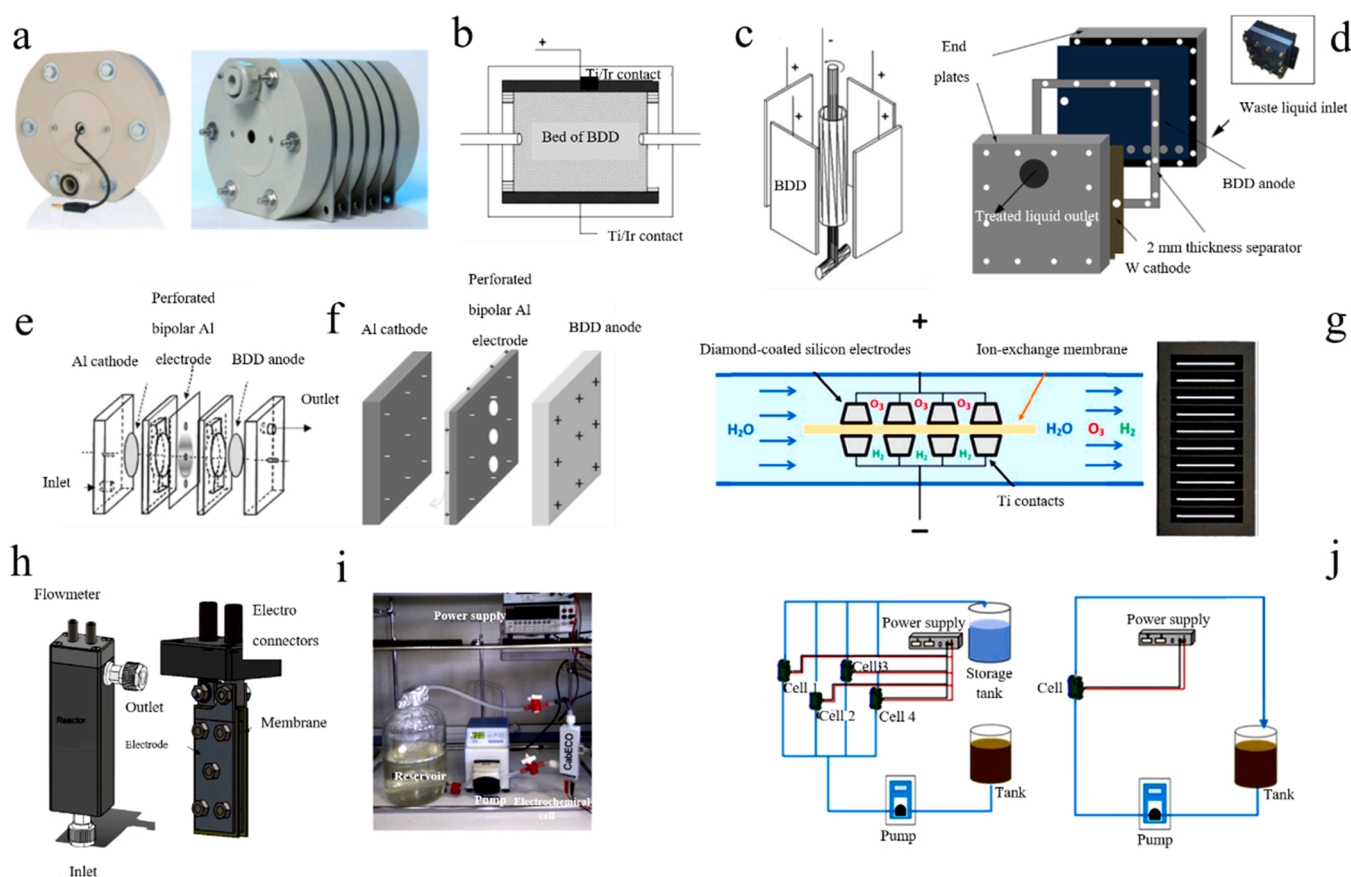


Fig. 29. Reactors with BDD anode used for electrochemical disinfection. Photograph of: (a) Diacell® 101, and (b) Diacell® 1001. Sketch of: (c) Cross section of a bed of BDD (volume near 0.4 mL). (d) disassembled typical filter-press reactor with picture of the assembled cell in the inset panel. (e) filter-press cell with 4 BDD sheets as anode surrounding a cylindric Ni cathode. (f) disassembled filter-press reactor with a perforated bipolar electrode. Electrochemical systems with undivided zero-gap reactors with BDD anode for O_3 production. Photograph of (h) CabECO® cell, and (i) experimental setup. (g) Left: Schematic depiction of the MIKROZON® membrane electrode assembly. Right: MIKROZON® electrode of structured silicon substrate with BDD coating on both sides. Schemes of (j) 4 MIKROZON® in continuous connected in parallel, and 1 MIKROZON® in batch mode.

(a) Adapted from [519]. (b) Adapted from [520]; (c) Adapted from [520]; and (d) Adapted from [523]. (e) Adapted from [524]. (f) Adapted from [521]; (g) Adapted from [522].

oxidation performances demonstrated by BDD anodes. Then, its actual applicability is a key challenge [192,517].

In some cases, these can be assembled by integrating numerous cell units, for example, Diacell® 1001 which can be also assembled with more than one Diacell® 101 modules (see Figs. 29a and 29b). These type of flow cells increase the electrode surface by typically connecting electrodes in bipolar configuration and, consequently, improving the EO efficiency for water disinfection or wastewater decontamination [517, 518].

As previously indicated, the innovations in the cell design and construction have been focused on different electrode configuration inside the cells such as 3D, multi-plates, and perforated electrodes. Under these conditions, high turbulence and more efficient mass transport conditions can be promoted inside the reaction-section cell, degrading more highly concentrated effluents or achieving greater inactivation percentages when operating at low electric charges. Recently, an undivided 3D flow reactor with diamond particles (Fig. 29c), filter-press flow cells with perforated bipolar electrodes (see Fig. 29f), and undivided flow cell with multi-anodic BDD plates with cylindrical cathodes (Fig. 29e) have also been reported [26]. Typical filter-press electrolyzers, are showed in Figs. 29d and 29f, which are flow cells extensively used at the laboratory.

Innovative commercial electrolyzers, based on flow-through electrochemical reactors, are CabECO® and MIKROZON® cells, which are illustrated in Fig. 29. These cells were assembled with a solid polymer electrolyte (SPE) and a polymer exchange membrane-electrolyte-electrode, which allowed to reduce the inter-distance between the electrodes, the use of several electrodes, the introduction of a polymer or membrane which favor the pre-concentration of pollutants and the gas formation and bubbles gases interferences are avoided as well as decrease the ohmic resistance, and consequently, reducing the energy requirements and process costs. In fact, the water matrices that will be treated act as the electrolyte in the cell, and consequently, its conductivity determines the cell voltage. Consequently, the addition of supporting electrolytes is recommended in great number of EO investigations for electrochemically treating synthetic or real water matrices [1,22]. In this context, on the one hand, the CabECO® cell is completely different (see Figs. 29e and 29f) because uses an SPE as electrolyte that connects directly the anodic and cathodic materials of the cell (zero-gap technology), thus allowing its efficient use to treat different water matrices with low conductivity. On the other hand, a structured silicon substrate and a double sided BDD coating (5 μm) are used (see Fig. 29g) in ten slots that allow the total contact area of membrane, BDD coating and water, which is crucial for O_3 production to higher removal efficiencies in both continuous and discontinuous operating modes (see Fig. 29h and 29i) with the MIKROZON® cell. This novel cell concept, in water disinfection, prevents the formation of chlorates. Then, the expected advantages by using flow-through cells with membrane technology are that the hydraulic residence time and the reduced electrode-gap favored a more efficient interaction between the electrochemically produced oxidants (ozone, chlorine, and persulfate among many others at the anode, as well as H_2O_2 by reduction of oxygen at the cathode) and the pathogen agents in the water.

5.4. Evaluation of TRLs and techno-economic assessment

Upscaling is one of the key tasks of process engineering, since it helps chemical and environmental engineers to understand the processes, which becomes a very important tool for their further optimization. This traditional concept has evolved significantly in recent years by spreading its view with a new scale, so-called TRL scale, which is not as related to the original chemical engineering core as the upscaling. The TRL scale is strongly related to the scale-up hierarchy and it has become one of the most relevant concepts in research in the recent years [73]. It allows individuating in a very simple manner: (i) the purpose of a research, (ii) the main actors who should be involved in its development,

and (iii) the distance covered from the initial idea and the pathway required to reach the destination [525].

Regarding the actors involved in each set of stages, they change importantly. The first stages of the TRL scale can be grouped into the category “ideas” (TRLs 1–3) and consist of preliminary studies confirming the technical feasibility of a new concept. In electrochemistry, these stages are typically covered by fundamental chemists or materials scientists using lab-scale facilities with focus on characterization techniques. After this, there is a second set of stages (TRLs 4 and 5) in which the process is developed by more applied scientists and engineers (e.g., chemical, electrochemical, environmental), trying to gradually approach to a more realistic situation from the previous results in which the idea was confirmed using different types of small prototype concepts. The goal is to give evidence on the applicability of the underlying idea. Here, the bench-scale plant is the main device, in which as it may be reminded, it is not the very different size of the components but the way of connecting them the key that characterizes the type of work and the information to be drawn. Then, a third set of stages (TRLs 6 and 7) needs the collaboration between companies and academics, trying to startup the manufacturing value chain validating the results obtained in the previous stages. To make more realistic the assessment, the use of pilot plant with cells, materials, and reagents close to those that should be used in the real application, is recommended. Interaction between academics and industrialists is the key to reach success. Note that the last stages of the TRL scales (TRLs 8 and 9) need the deep involvement of companies and, here, the contribution of academics is much less important. At this point, it is not so relevant to deeply understand the system but to make it work in the most efficient way by starting the real production. Here, real prototypes are the key. Hence, if deeply compared, there is an almost direct correspondence between the classical theory of scale up and the TRL scale because the size and feasibility of the facility corresponds to the purpose of the evaluation. From these comments, it can be deduced that level 1 is typically correlated with lab-scale, level 2 with bench, level 3 with pilot and level 4 with real prototypes. However, the definition of the actors that should participate in each level is one of the most important contributions of the TRL concept. Research should combine the efforts of the academic and industrial worlds, but the tools of these two worlds are very different and there is a critical level in which interactions between both communities should be enhanced.

Most of the existing challenges are derived from the low TRL studies (i.e., TRL 1–3), in which the ideas start to emerge. The development of new electrodes and coatings with different formulations, as well as the design of new homogeneous and heterogeneous catalysts have been a continuous source of new knowledge for the degradation of organic pollutants in the last six years. This clearly contrasts with research made in previous decades [526]. This is reflected in an increasing number of works regarding the MMO anodes for EO [68,70,147,455], since the applications need to incorporate electrodes as cheap as possible. In this regard, a feasible target can be the obtention of robust and efficient electrodes with average costs below 100–200 € m^{-2} , although the price do not only depend on the coating but also on the substrate and manufacturing procedure. These values are much below the current market price for lab studies (with electrode dimensions of only 1–300 cm^2 , whose cost is exactly in the same range), but they are attainable according to current large scale production processes. Their oxidation power can be enhanced upon combination with other AOPs like UV photolysis or sonolysis, reaching high mineralization rates and efficiencies. Their use can also bring paradigmatic changes in the application of electrochemical technology to water treatment [72]. Perhaps, one of the most promising concepts, but still at a very low TRL, is the transformation of the electrochemical wastewater treatment into an electro-refinery, in accordance with the new paradigm of circular economy. Recent works are pointing out the necessity of reevaluating the treatment of wastes, not as a method for the destruction of organics but as a method of producing new resources that can help to reduce the

consumption of raw matter and energy [527–529]. This means that the actual cost of the electrochemical treatment of wastes could be dramatically reduced, eventually generating revenues. In the case of EO, operation costs (i.e., around 50% of total costs [530]) were set in the range of 10–50 € m⁻³ more than a decade ago; however, there is a lack of studies reporting current treatment costs, with the exception of some rough estimations made from too simplistic lab-scale studies. In recent years, it is surprising the high growth rate of techno-economic studies, which has not been encompassed by a deep discussion on the significance of such analysis. The authors of some very rigorous evaluation, made at lab scale, suggest that nothing has changed regarding the understanding and reporting of economic aspects, in spite of the gradual increase of technical knowledge on water treatment technologies in the last decade [531].

Pioneering works trying to transform conventional waste treatment systems into factories able to produce energy or value-added chemical were related to microbial fuel cells, in which wastewater is used to produce energy as it is simultaneously decontaminated [532–534]. Some microbial electrolyzers were developed to reduce the energy consumption thanks to the production of hydrogen [532]. The use of RED stacks for autonomous wastewater treatment is another interesting application in this regard (see Section 3.3.2) [535]. Moreover, the utilization of assisted RED was provided to reduce the energy consumptions [535,536]. There are also several works focused on the production of valuable materials such as carboxylic acids, which are formed following the oxidative degradation of aromatic pollutants [537]. The main challenge is the purification of the products manufactured. The development of new coatings is also a point to be more largely evaluated in the next years, trying to influence on the selectivity of the reactions to transform pollutants into high-added value products (similarly to the electrosynthesis concept) [189,538], instead of mineralizing them [539]. Regarding the bioelectrogenic systems, despite the very high number of manuscripts published in the last two decades, the difficulties in the real scale-up, and a stabilization of the maximum amounts of energy which can be produced, have questioned their real added-value with the present knowledge (opposite to their very promising status dating back one decade) [540]. Except for miniaturization, in which the scale up is attained by replication [541,542], it is not clearly seen as a promising application to provide high amounts of energy from the treatment of wastewater [543].

Regarding the first intermediate level (i.e., TRL 4–5), the destruction of selected pollutants from different types of matrices is the main purpose, trying to elucidate the mechanisms in the lower stages and the effect of interferences and other species in the higher ones. At these levels, in the last years, it can be noticed that changes in the formulation of wastewater by adding salts to increase the conductivity are started to be seen more a problem than a viable solution [73]. This addition significantly increases the operation costs and changes the type of pollution, from more hazardous (anthropogenic organics) to more persistent (salts), as high salinity is nowadays considered a problem with no evident solution. This trend is opposite to the significance of the formulation of the absorbent/electrolyte in the electro-scrubbing of gases, where the addition of salts that promote the production of oxidants is a key point, although in this later case the liquid is continuously regenerated and recycled instead of being discharged as a liquid waste [544]. The combination of cells for the sequential concentration and treatment of pollutants is also a topic that has started to be studied recently, considering that the efficiency of the electrochemical treatments usually depends on the concentration as they fit well to first order kinetic models. Hence, the use of coagulation/electrocoagulation for the concentration of colloidal pollutants [545–547], or the ultrafiltration of these colloids [548], electrodialysis for the concentration of ionic pollutants [549,550] and granular activated carbon combined with methanol desorption for the case of soluble organics [551,552] have been evaluated recently. Regarding the second intermediate level (i.e., TRL from 6 to 7), testing real applications with the collaboration between

companies and academics leads to synergisms that allow scientist to benefit from the most recent innovations of companies, whereas it allows companies to give an added value to their product. Production of oxidants [553], removal of pollutants [519,554] and, especially, the development of electrodisinfection devices [523] constitute a source of revenues for many companies. Companies are then more interested in testing their commercial devices in order to open markets in which they could be become a promising option. Regarding last level, very few collaborations in the context of electrochemical treatment of wastewater are fully successful. Furthermore, there is not always interest or option to disseminate the results because of the conflict of interest with the company, which reduces the number of published papers. Patents would be the key at this level; although some comments will be made in the next subsection, it can be commented that there is not a direct correlation between the number of patents and, from one side, the real application of the electrochemical technology for wastewater treatment and, from the other side, the number of high quality papers published. It is in the last set of stages of the TRL scale where economy becomes a key topic and the value chain is sufficiently mature to have an accurate value of the different items because scale economy can be considered properly. However, regarding diffusion, cost analysis remains as an unsolved problem. Many attempts are being carried out, but comparison is still difficult considering that most of the information comes from academics and not industrialists, which are not especially interested in disseminating this type of information. There is an arbitrariness in those studies and, perhaps, a bias that makes most of them useless. This is mainly related to the source of the data used in these studies. It is not realistic to use data obtain at lab scale to make even a preliminary estimation of costs. Also, the bench scale can only be used for very preliminary evaluations that allow making a rough estimation of costs. Because of the scarcity of tests at the pilot-plant scale, reliable information needed for a serious economic analysis is not available. Tools like life cycle cost (LCC) are expected to help in the next years to solve this problem [158]. These tools are also related to other important tools that also belong to the last set of TRL stages, the life cycle assessment tools (LCA). Sustainability is one of the main challenges of humankind in the next years and the assessment of important concepts such as the carbon and hydric footprints of electrochemical water treatment processes is needed in order to make progress in this topic in accordance with circular economy policies [471,555–558]. It can not only be suggested, as it is already done in a very high percentage of the recently published manuscripts, that electrochemical technologies are green, but it is important to demonstrate it by stating how the powering with green energies can be made and contribute to making the technology clean. However, results published demonstrate that this is not as simple as connecting the green power supply with the electrochemical cell, and that many options must be considered regarding the influence of the continuous or interrupted powering and the use of energy storage devices [558–562]. Thus, it is important to include LCC and LCA analysis in electrochemical processes, but at present this is only addressed in a light manner and, as pointed out recently, it deserves more attention in the future [563].

5.5. Patents

Unfortunately, a patent is not always related to a real innovation, but it can serve to legally preserve the use of a technology and, sometimes, a way to publicize an expertise on a given topic. Because of that, much of the most important progress in innovation is not protected under this legal concept but it is simply kept as a secret know-how of industrialists/manufacturers. For this reason, a large part of the existing patents is completely irrelevant and might have serious difficulties to demonstrate enough relevance under a deep assessment, despite of their legal validity. This explains why a simple search with a general internet search engine tool like Google Patents yields more than 27,000 results related to the concept “wastewater treatment electrochemical cell” since January 2010, out of which more than 13,000 have been published since

January 2015. These documents refer to patents in one or several of the 175 patent offices considered, meaning that the same patent can count several times if it has been registered in many different offices, as it is commonly made. Regarding the topics, they range from the applicability of “masked” well known cells for hundreds of different and specific purposes to slight modifications of conventional cells with a validity that could be, at least, questionable. The proof of this imbalance between number of patents and actual technology is that the number of successful electrochemical devices is quite limited. Thus, the number of patents may give a distorted view of reality. Thus, a simple search of marketed technology with the internet search tool Google.com confirms this point, because of the very small number of companies offering real wastewater treatment solutions at TRL 8–9 based on electrochemical technology.

As for the origin of the patents, it is interesting to see how the largest number of patents comes from southern Asia countries (considering the 175 patent offices whose data are collected for the referred application). Since January 2015, the same concept previously used (“wastewater treatment electrochemical cell”) has yielded around 1200 results from the world patent office, more than 1300 from United States, 600 from the European Patent Office and 7300 from China, 900 from South Korea and 1800 from Japan. On the other hand, considering the home countries of the authors of this review, the number decreases to only 111 from Brazil, 66 from Spain and none from Italy. It is true that these figures reflect a higher or lower industrial interest, competitiveness and activity, but comparison with scientific publications, as for Web of Science or Scopus, reflects that scientific knowledge and value-added applications do not always walk together and the TRL scale is not working properly. For example, a comparison with Scopus in the same period yielded a number of papers of 1130 (China 370, US 140, Spain 113, India 112, Australia 58, Italy 50, Brazil 46, South Korea 43 and Japan 10). This is a tricky problem because in scientific literature relevant innovation often is not published, whereas the relevant innovation that can be found in the patents is hardly contrasted.

Regarding the most interesting topic found in patents, worth highlighting are those related to changes or new development in the mechanical design of cells. An example is US20170283283A1 (Electrochemical system and method for the treatment of water and wastewater), which was also presented in many other offices with other references, with great efforts being made in reducing interelectrode gap and improving electric power feeding. Another interesting example is EP3402752B1 (Electrochemical cell for wastewater treatment with increased removal rates of pollutants) which is an example of cell containing polymer electrolyte membranes, improved current collection and cell compression system. As well CN212127844U (Electrochemistry sewage treatment device), in which adsorption is used to improve the results obtained by the single electrochemical process. A last highlighted example comes from a Canadian patent in which an electrochemical cell can be equipped with flat-sheet, spiral-wound, or hollow-fibre arrangement of a multi-electrode array and the cell includes one or more gas diffusion electrodes that are permeable to a gas but impermeable to water (CA2836687A1, Electrochemical cell for water treatment). As observed, all these cells are focused on topics that are widely suggested but not exhaustively studied in the scientific literature, being many of them highlighted as challenges in the previous sections. However, there is a lack of patents related to other important aspects that require further improvement, such as the use of increasing operation pressure to promote the formation of oxidants like H_2O_2 or O_2 thought an increase in the availability of reagents taking into account that solubility of gases increases linearly with pressure, as it has been also pointed out in previous scientific works [469,564]. Also worth highlighting is the adaptation of cells components of the whole cell for applications that differ from those for which they were initially developed. However, in the patent search, as well and in the scientific literature search, real challenges that were pointed one decade ago are still missing [439], and little effort seems to be done. Thus, taking advantage of 3D printing and CFD modelling could lead to a more efficient design

and manufacturing of cells, additionally reducing the cost of electrochemical cells. Although there is a lack of reports with updated prices, the last reference to Williams equation yielded values of $\sim 20000 \text{ € m}^{-2}$ with an exponential factor of 0.78 [530], being the range of applicability of this equation up to 15 m^2 . As stated above, the lack of rigorous techno-economic assessments is becoming a real problem in the field, since researchers find it difficult to evaluate the maturity of their inventions for practical applications. Likewise, this drawback supports the reluctance of companies to approach the research centers where the technology is being developed. A recent work focused on a small setup reported values in very close agreement with the predictions made by the Williams equations a decade ago [531].

5.6. Powering the electrochemical devices with green sources

One of the most important promises for the application of electrochemical technology to the treatment of water and wastewater is its sustainability, which can be greatly improved by their powering using green energy sources [62]. The main requirement of electrochemical processes is electricity, and there has been a very rapid development of technologies capable to transform renewable sources into electricity, among which photovoltaic panels and wind turbines seems to be the most important, but there are many others with still very few works carried out, such as hydraulic mini turbines or piezoelectric devices. However, there are many other options that should also be accounted looking for a more sustainable way of application of the electrochemical technology. In a previous subsection, it was mentioned that the bio-electrochemical devices were seen as a very promising option two decades ago, based on very optimistic calculations that forecast the substitution of conventional biological processes by microbial fuel cells to save the important power requirements for the aeration of the biological reactors. In addition, they were expected to harvest huge amounts of energy that could be supplied to the electric grid, contributing to a more sustainable progress [540]. However, after thousands of papers, scale up was found to be more difficult than planned [543], and now it seems clear that they have no real promising applications at large scale, although they can be still promising when miniaturized for powering small devices [542]. Perhaps, soil microbial fuel cells represent an alternative to microbial fuel cells where the liquid electrolyte is substituted by polluted soil, making possible their scale up, even when more studies should be performed to boost the electricity production [565,566].

Important advances have been made in relation with the direct application of electric power produced by renewable energies to electrochemical wastewater treatment processes. The time-dependence of the power produced was found to be not as important as in soil electrokinetic remediation, in which low power production periods (e.g., at night for systems relying on PV solar energy) may revert the mobility of pollutants and lead to less efficient processes [567,568]. The treatment of organics is based on almost irreversible reactions and hence, the loss of efficiency because of the reversal of processes in the absence of power is not observed. However, there is an influence, and it was found that when powering green energies, energy management is the most relevant challenge to optimize the energy supplied. Thus, per power unit obtained by the green source, the amount of pollutant removed from a given wastewater can be optimized [515,555,560,569]. In this context, very promising results are obtained through digitalization, that is, by combining data management with the target of the treatment by forecasting weather conditions to try to fit the demand and the production in the most efficient way.

Another interesting topic related to sustainability is the transformation of a problem into an advantage. One of the products associated to the electrochemical treatment of wastewater is hydrogen, produced by the cathodic reduction of water on the surface of the cathodes. The amounts produced are very low to obtain a reasonable payback of the investment necessary to store and produce electricity

again. However, in full-scale processes they are high enough to compromise safety and it should be properly managed. This opens a new possibility in the use of green hydrogen, produced during electrolytic wastewater treatment processes, in gas-to-power strategies by pumping it into gas pipelines to be valorized energetically (see also comments in subsection 4.4). The recently proposed use of salinity gradients to sustain the electrochemical treatment of wastewater by means of RED stacks is also worth highlighting (see Section 3.3.2). In particular, some groups have shown that it is possible to use river, seawater and/or brine solutions to treat various kinds of wastewater both in lab-scale devices [253,254,256,570] and in a pilot-plant scale [258]. In this frame it has been observed that the plants devoted to the treatment of industrial wastewater deal often with waters characterized by different salinity and their salinity gradient can be used to depurate part of these wastewaters by RED, allowing potentially a relevant saving of energy [42].

5.7. Case studies

There are very few applications reported in the scientific literature about real full-scale applications of the processes reviewed in this paper, partly due to the lack of interest of high impact journals because of the low relevance in terms of fundamental knowledge progress. Innovation is seen as a mayor barrier. However, it would be very important for the development of the technology to highlight those applications and the important points that should be addressed during their development, such as the training of workers, integration of technologies, information to stakeholders and relevance of the complete value chain, among others. Large projects funded by supranational organizations (like the recent European H2020 or the Life Program calls) have aimed to develop the necessary value chains by establishing consortia partnering academics and companies. A very interesting example is the outcome of Safewaterafrica project (<https://cordis.europa.eu/article/id/415837-new-technology-provides-clean-water-in-africa>), performed by a consortium of 13 partners from Europe (Germany, Italy, Spain) and Africa (South Africa and Mozambique) in which two prototypes were commissioned and operated for more than one year in Southern Africa to provide safe water to rural communities. This experience has allowed to scale-up the CabECO® electrolyzer technology (a PEM electrolyze, which promotes the formation of ozone using diamond electrodes manufactured in series by the German company CONDIAS) [523], and integrated it with electrocoagulation throughout a new process called PREDICO [571,572] and other more conventional technologies such as nanofiltration, being all this system powered with PV solar panels [573, 574]. Gained experience about real problems faced when treating actual wastewater of very low quality and about how the full value chain of the technology must be developed are important outcomes of this project and worth to be evaluated for future full-scale applications. Unfortunately, there is a lack of information in the scientific literature about this project and many other similar because integration of technologies and the conformation of the value chain is not in the core of the interest of the scientific literature, although it is a key point to be considered if electrochemical technologies for the degradation of organic pollutants aims have to become a reality in the near future.

6. Concluding remarks

Electrifying the energy and transportation sectors is one of the strengthened strategies devised in recent years by governments all around the world for the transition towards a decarbonized society. At the same time, the need to provide effective processes for the remediation of aqueous effluents generated by industrial and civil sectors is fundamental to achieve a more sustainable economic development and to contrast the dramatic problem of water scarcity. This review aligns well with these topics, critically discussing the main existing alternatives for developing electrified water treatment technologies.

Until some decades ago, the applications of electrochemistry could

be regarded as quite restrictive and specialized, being only viable for certain industrial processes like the chloralkaline one. Nonetheless, the price of electricity in many countries is no longer prohibitive, owing to the introduction of renewable energies. Lately, the coupling of solar photovoltaics has demonstrated the feasibility of solar-driven electrochemical water treatment, which could be extended to other clean energy sources like wind or clean energy vectors such as green hydrogen. The exploitation of salinity and thermal gradients, especially in facilities located in estuaries or with unused waste heat, can also serve to power the electrochemical reactors. Moreover, electrochemical process can potentially use the peaks of electric energy production, which are characterized by very low (or even negative) prices, to reduce their cost. Several coupled processes that rely on these approaches have been discussed here. The resulting technologies have increased their eco-friendliness, minimized the generation of secondary pollutants and decreasing the energetic requirements, and reduced their cost, which combined with their ability for in situ effective production of powerful oxidants and reductants, allows them climbing up positions in the complex and competitive market of the water sector. Moreover, it has been shown that in many cases electrochemical routes are more effective than the corresponding chemical ones. In particular, in this review, the most interesting innovations and findings reported in the last seven years have been selected and critically discussed (i.e., about 450 publications selected among more than 7000 found in the literature). In the near future, a more intense upscaling of some of the most promising reviewed processes will be mandatory to get a larger range of case studies in order to break the reluctance of potential stakeholders and end-users to electrochemical technology and increasing in this way the technology readiness level of electrochemical wastewater treatment technologies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.122430](https://doi.org/10.1016/j.apcatb.2023.122430).

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Glossary

- AO: anodic oxidation
 AOP: advanced oxidation process
 ATP: adenosine triphosphate
 BCNW: boron-doped vertically aligned graphene walls
 BOD₅/COD: biodegradability index (i.e., ratio between biological and chemical oxygen demand)
 BDD: boron-doped diamond
 c₀ and c_f: initial and final concentrations of the organic pollutant or COD values, respectively
 CE: current efficiency
 CF: carbon felt

CFD: computational fluid dynamics
CFU: colony forming units
CNT: carbon nanotube
CO₂RR: CO₂ reduction reaction
ΔG: variation of Gibbs free energy
D: diffusivity
D_{||}: gas diffusivity parallel to catalyst surface
DEMS: differential electrochemical mass spectroscopy
DET: direct electron transfer
DF: diamond fiber
DFT: density functional theory
DMPPO: 5-Dimethyl-1-pyrroline-N-oxide
DOC: dissolved organic carbon
DSA: dimensionally stable anode (registered trademark)
EAOP: electrochemical advanced oxidation process
E_{cath}: applied cathode potential
E_{cell}: potential difference between the anode and cathode
ECH: electrocatalytic hydrodechlorination
EC_v: energy consumption per unit volume
ED: electrodialysis
EDDS: ethylenediamine-*N,N'*-disuccinate
EDX: energy-dispersive X-ray spectroscopy
EDTA: ethylenediaminetetraacetate
EF: electro-Fenton
EO: electrochemical oxidation or electrooxidation
ER: electroreduction
ESR: electron spin resonance
FAC: floating air cathode
FESEM: field-emission scanning electron microscopy
GDE: gas-diffusion electrode
GDL: gas diffusion layer
HAA: haloacetic acid
HER: hydrogen evolution reaction
HOMO: highest occupied molecular orbital
HPLC: high-performance liquid chromatography
k_m: mass-transport coefficient
I: current
i or *j*: current density
i_{lim}: limiting current density
I_{appl}: applied current
i_{appl}: applied current density
IEO: indirect electro-oxidation
IL: ionic liquids
LCA: life cycle assessment tools
LCC: life cycle cost
LDH: layered double hydroxides
LMCT: ligand-to-metal charge transfer
MIL: materials Institute Lavoisier
MMO: mixed-metal oxide
MO: metal oxide
MOF: metal-organic framework
MWCNTs: multi-walled carbon nanotubes

NADE: natural air-diffusion electrode
NCD: nanocrystalline diamond
NOM: natural organic matter
NPs: nanoparticles
NTA: nitrilotriacetate
ORR: oxygen reduction reaction
PEC: photoelectrocatalysis
PDS: peroxydisulfate
PEF: photoelectro-Fenton
PES: potential energy surface
PFAS: perfluoroalkylated substances
PFDA: perfluorodecanoic acid
PFNA: perfluorononanoic acid
PFOA: perfluorooctanoic acid
PFOS: perfluorooctane sulfonate
PIM: polymers of intrinsic microporosity
PVA: polyvinyl alcohols
PTFE: polytetrafluoroethylene
Q: electric charge
RCE: rotating cylinder electrode
RCS: reactive chlorine species
RDE: rotating disk electrode
RED: reverse electrodialysis
RHE: reversible hydrogen electrode
ROS: reactive oxygen species
RRDE: rotating ring-disk electrode
RVC: reticulated vitreous carbon
SAA: single atom alloys
SAC: single atom catalyst
SCC: single cluster catalyst
SDG: sustainable development goals
SEM: scanning electron microscopy
SHE: standard hydrogen electrode
SPE: solid polymer electrolyte
SPEF: solar photoelectro-Fenton
SS: stainless steel
STEM: scanning transmission electron microscopy
THM: trihalomethane
TN: total nitrogen
TOC: total organic carbon
TON: turnover number
TRL: technology readiness level
TSS: total suspended solids
UNCD: ultrananocrystalline diamond
UV: ultraviolet
WC: Wenzel-Cassie
WHO: World Health Organization
VOC: volatile organic compounds
WWTP: wastewater treatment plant
ZIF: zeolitic imidazolate frameworks
ZVI: zerovalent iron